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Contents

	Page
The Evaluation of the Intrinsic Viscosity (as Intrinsic Flow Time) of GR-S in Benzene— <i>L. H. Cragg, T. M. Rogers, and D. A. Henderson</i> - - - - -	333
A Note on the Variation with Temperature of the Intrinsic Viscosity of GR-S in Benzene— <i>T. M. Rogers, D. A. Henderson, and L. H. Cragg</i> - - - - -	351
The Growth of La^{140} (40 hours) from Ba^{140} (12.7 days)— <i>W. E. Grummitt, J. Guéron, G. Wilkinson, and L. Yaffe</i> - - - - -	357
The Fission Yields of Ba^{139} and Ba^{140} in Neutron Fission of U^{235} and U^{238} — <i>W. E. Grummitt, J. Guéron, G. Wilkinson, and L. Yaffe</i> - - - - -	364
Fission Yields of Masses 131, 132, 134, and 136 Formed in Neutron Fission of Uranium— <i>L. Yaffe and C. E. Mackintosh</i> - - - - -	371
The Synthesis of Some Carbazole Derivatives— <i>Richard H. F. Manske and Marshall Kulka</i> - - - - -	376
The Preparation, Purification, Physical Properties and Hydrolysis of Cyanogen Chloride— <i>D. E. Douglas and C. A. Winkler</i> - - - - -	381
Studies on the Formation of Hexamine— <i>Mary L. Boyd and C. A. Winkler</i> - - - - -	387
A Recording Unit and Electronic Shunt Selector for a Mass Spectrometer— <i>F. P. Lossing, R. B. Shields, and H. G. Thode</i> - - - - -	397
The Kinetics of the Formation of Ethanolamines— <i>C. Potter and R. R. McLaughlin</i> - - - - -	405
The Kinetics of Consecutive Second Order Reactions— <i>C. Potter and W. C. Macdonald</i> - - - - -	415
Fractionation of the Reaction Product of Linseed Oil and Glycerol— <i>J. G. Breckenridge and J. H. E. Herbst</i> - - - - -	420

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THE EVALUATION OF THE INTRINSIC VISCOSITY (AS INTRINSIC FLOW TIME) OF GR-S IN BENZENE¹

BY L. H. CRAGG,² T. M. ROGERS,³ AND D. A. HENDERSON⁴

Abstract

From careful measurements of the relative flow times of solutions of GR-S in benzene, it has been established that the intrinsic flow time (and hence the intrinsic viscosity) of GR-S in benzene may be most precisely determined by the use of a function $n(t_r^{1/n} - 1)/c$, based on the Baker equation relating η_r , the relative viscosity, and c , the concentration; for the GR-S - benzene system the value of n may be taken as 8. For the greatest precision $[t]$ is determined by linear (horizontal) extrapolation, to zero concentration, of the 8 $(t_r^{1/8} - 1)/c$ vs. c plot; in rapid routine work $[t]$ may be evaluated as 8 $(t_r^{1/8} - 1)/c$ by measurements on only one solution of a concentration such that $t_r = 1.8 \pm 0.4$.

The importance of the intrinsic viscosity $[\eta]$ of a high polymeric substance, as a function empirically and theoretically related to the average chain length of its molecules (34), is now thoroughly established. When the polymeric substance consists of the linear members of a homologous polymeric series (6, 18), intrinsic viscosity is a simple function of the average molecular weight

$$[\eta] = \alpha + KM^\nu, \quad (1)$$

where α is negligibly small for *high* polymeric substances (21), and ν is a constant* related to the axial ratio of the molecules (32). Therefore $[\eta]$ is important both in careful studies of the size and shape of high polymer molecules and for following in a routine way the course of various polymeric reactions. For purposes of research, methods of evaluating $[\eta]$ should be accurate; for routine control, they should be rapid and fairly precise. Several methods are widely used at the present time but in both respects they leave a good deal to be desired.

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ont. This paper has appeared as a confidential report, dated August 20, 1946, to the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada.

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* If $\nu = 1$, as implicitly assumed by Staudinger, M is the weight average molecular weight; if, as is more usual (25, p. 146), $\nu \neq 1$, M is the 'viscosity average' molecular weight (16), or 'the average for ν equal to a certain value' (22).

Intrinsic viscosity is a limiting function. Various definitions, such as $\lim_{c \rightarrow 0} \eta_{sp}/c$, $\lim_{c \rightarrow 0} \frac{\ln \eta_r}{c}$, $\lim_{c \rightarrow 0} \frac{d \eta_r}{dc}$,* have been shown to be equivalent (11); they all emphasize the fact that ultimately $[\eta]$ must be evaluated by an extrapolation to zero concentration.

Most commonly $[\eta]$ is determined graphically from a plot of either η_{sp}/c or $\frac{\ln \eta_r}{c}$ against c , on the assumption that these curves are linear in the low concentration range; sometimes η_{sp}/c is plotted against η_{sp} (22, 31) or $\frac{\ln \eta_r}{c}$ against η_r (23), and the curve extrapolated; much less frequently η_r is plotted against c , the curve extended to $c = 0$, where $\eta_r = 1$, and the tangent drawn to the curve at that point. The assumption that η_{sp}/c is a linear function of c at very low concentrations, originally made by Staudinger (33, pp. 56 ff.) (and, as we have seen, used as the basis of a standard method of evaluating $[\eta]$), has been justified on theoretical grounds by Huggins (21), and by much experimental work. Relatively accurate extrapolation should therefore be possible. Unfortunately, however, the relation is often linear only at concentrations where precise measurement of η_{sp}/c is impossible;† at higher concentrations deviation from linearity may become marked, especially as $[\eta]$ increases (9). Similar considerations apply to the $\frac{\ln \eta_r}{c}$ vs. c plot, although it has the advantage that $\frac{\ln \eta_r}{c}$ is less dependent on c than is η_{sp}/c . With the advantages of linear extrapolation in mind many investigators have searched for relations between relative viscosity and concentration that would be linear over a wide range. Many equations have been proposed in the last 15 years; they have been compared and evaluated by several authors, perhaps most thoroughly by Hess and Philippoff (19) and by Martin (26). Huggins (21) demonstrated that most of these equations (those proposed by Baker (2), by Fikentscher and Mark (14), by Schulz and Blaschke (31), by Bungenberg de Jong, Kruijff and Lens (5), by Martin (26), by Arrhenius (1), by Hess and Philippoff (19), and by Bredée and de Booy (4)) reduce at very low concentrations to an equation of the form

$$\eta_{sp}/c = [\eta] + K' [\eta]^2 c, \quad (2)$$

the equation which he had arrived at on theoretical grounds. In practice the equations proposed by Martin and by Baker seem to be most widely suitable. Baker's equation (in our notation)

$$\eta_r = (1 + ac)^n, \quad (3)$$

where a and n are constants, has been much used in studies of cellulose and its derivatives, especially in the form given it by Philippoff and Hess (19, 29)

$$\eta_r = \left(1 + \frac{[\eta]}{8} c\right)^8. \quad (4)$$

* In these expressions $\eta_r = \eta/\eta_0$ (the viscosity of solution relative to that of the solvent under the same conditions), $\eta_{sp} = \eta_r - 1$, and c is the concentration expressed (11) in the units grams solute per 100 ml. solution. $[\eta]$ therefore has the dimensions of a specific volume and is expressed in the units dl./gm. (12).

† As c becomes very small, η approaches η_0 in value and the difference $\eta_r - 1$ becomes very small; under these circumstances, therefore, η_{sp}/c is a ratio of two small quantities.

The equation is however more versatile as originally proposed, for the adjustable constant n makes it possible to adapt the equation to any polymer-solvent system. For our purpose it is more useful in the equivalent form

$$\eta_r = \left(1 + \frac{[\eta]}{n} c\right)^n \quad (5)$$

The Martin equation

$$\log \eta_{sp}/c = \log [\eta] + K [\eta] c, \quad (6)$$

is closely related to that originally proposed by Bungenberg de Jong, Kruyt and Lens and used by Staudinger (35) in the form

$$\begin{aligned} \log \eta_{sp}/c &= \log [\eta] + K_{st} c \\ &= \log [\eta] + (K_{mat} + b) c \end{aligned} \quad (7)$$

but it has the advantage that it eliminates the second constant b . As a result of a graphical comparison of the various equations Martin (26) has concluded that his is the one most generally suitable, and the plot to be preferred for the determination of $[\eta]$ is that of $\log \eta_{sp}/c$ vs. c . Howlett, Minshall, and Urquhart (20), on the other hand, concluded from a very thorough study with data on cellulose in cuprammonium that the Baker equation was the best of those available. They used it in the form

$$\eta_r^{1/n} = 1 + \frac{[\eta]}{n} c \quad (8)$$

and showed that when $n = 8$ the data gave a straight line over a wide concentration range.

In our experience with the synthetic rubber GR-S (in benzene) the most commonly used methods of determining $[\eta]$ by graphical extrapolation were disappointing. The work of Howlett *et al.* and of Martin encouraged us to undertake a comparison of various methods as applied to the GR-S-benzene system.

Experimental

Materials

The rubber used was a sample of normal commercial GR-S obtained from Polymer Corporation, Sarnia, on October 27, 1945. It was gel-free when received and, stored in air in the dark, remained so during the period of experimentation. In the experiments reported here the GR-S was not extracted with the ethanol-toluene azeotrope to remove non-rubber constituents as we were more interested in the behaviour of GR-S as ordinarily used, but preliminary tests satisfied us that these constituents did not affect the viscosity of the rubber other than by acting as a simple diluent.

* When c is very small, Equation (3) reduces to $\eta_r = 1 + nac$.

Hence
$$\left(\frac{d\eta_r}{dc}\right)_{c \rightarrow 0} = na = [\eta], \text{ and } a = \frac{[\eta]}{n}.$$

It is interesting to note that Baker used the constant 'na' to characterize polymer-solvent systems 25 years before the name 'intrinsic viscosity' was introduced and almost 20 years before Staudinger and others demonstrated the importance of the limiting reduced viscosity.

It should be noted that Baker expressed concentration in the units grams per 100 cc. solution, Philippoff in grams per 100 gm. solution (see reference 29, pp. 168-169). Except when the density of the solvent is unity, then, Philippoff's $[\eta]$ is not strictly speaking the intrinsic viscosity as we define it (11, 24).

The solvent used was technical benzene (obtained from the Steel Company of Canada, Hamilton) freed from thiophene by extraction with concentrated sulphuric acid and purified by fractional distillation. The material used boiled in the range 80° to 80.5° C. and gave a negative test with isatin.

Apparatus

Viscosities were determined from measurements of flow time in an Ostwald - Cannon-Fenske capillary viscometer, A.S.T.M. No. 50. This type of viscometer was chosen for use because it is rugged, relatively inexpensive, readily available, and in wide use for routine viscometry. The particular instrument used had the following characteristics:

L , length of capillary, measured	7.3	cm.
R , radius of capillary,*	0.022 ₂	cm.
H , mean hydrostatic pressure head (loading volume, 10 ml.)	8.95	cm. (head at $t/2$ sec.)
t , time of efflux at 25° C.		
for benzene	171.0	sec.
for water	220.5	sec.
V , volume of efflux (vol. between marks)	3.25	cm. ³

Whence:

$$LT/V \text{ (for benzene)} = 3.84 \times 10^2$$

$$HR/L = 0.027$$

$$\tau, \text{ mean shearing stress at the wall } (HdgR/2L), = 11.7 \text{ dynes per cm.}^2$$

The viscometer was therefore of such dimensions that the kinetic energy correction is small enough to be neglected in routine work (the error in intrinsic viscosity caused by neglecting it was found to be of the order of 2%), and the mean rate of shear falls within the range accepted arbitrarily as standard for determining the intrinsic viscosity of GR-S in benzene (15). The charging volume of liquid, 10.0 ml., was measured in a pipette, the same pipette being used for every loading. For measurements of relative flow time t , (the ratio of flow time of solution to that of solvent at the same temperature) the actual volume loaded need not be known exactly so long as it is kept constant. (With a constant charging volume of 5 ml., the relative flow time is the same, within experimental error, as with one of 10 ml.) The effect on the volume of differences in rate of draining from the pipette was proved to be insignificant over the range of concentrations employed.

Temperatures were controlled by means of a constant temperature bath, which consisted of water in a 12 by 12 in. cylindrical Pyrex jar heavily lagged with asbestos (through which windows were cut for observation). The bath was provided with an efficient stirrer, a cooling coil, and a heater controlled by a thermoregulator of the de Khotinsky type protected by an electronic

* Calculated from the Poiseuille formula, $\eta = \pi R^4 H g d t / 8 L V$, using the following values: $d_{25} = 0.873 \text{ gm./ml.}$, $\eta_{25} = 0.00603 \text{ poise}$, $g = 981 \text{ cm./sec.}^{-2}$

relay; by these means the temperature was kept uniform throughout the bath liquid and constant to $\pm 0.01^\circ \text{C}$. The viscometer was supported on the edge of the jar in correct vertical alignment by means of a specially designed clamp. Measurements of temperature were made with a calibrated thermometer; and the flow times were measured with a calibrated stopwatch read to 0.1 sec.

Procedure

Solutions were prepared by dissolving weighed samples of GR-S in benzene and then making the solution up to volume; concentrations are therefore expressed as gm. per 100 ml. solution. A portion of GR-S was cut into cubes (approximately 1 mm.³), the desired amount weighed to 0.1 mgm., introduced into a dry 100 ml. volumetric flask, covered with 90 ml. solvent, and allowed to stand undisturbed in the dark for 24 hr., whereupon solution was complete. (Since the polymer was gel-free the solution was not filtered except when extraneous material was obviously present.) The solution was brought to $25.00 \pm 0.01^\circ \text{C}$. by suspending the flask in the bath for at least 10 min., and then, after gentle but thorough mixing, benzene at the same temperature was added to a total volume of 100.0 ml.

Measurements of flow time were made in duplicate or triplicate with each loading and repeated on successive loadings until agreement within ± 0.1 sec. was obtained. At regular intervals the flow time of pure solvent was redetermined to make sure that no particle had lodged in the capillary. After each run the viscometer and pipette were cleaned with benzene, by filling and emptying twice and then flushing thoroughly, and dried with air filtered through absorbent cotton and a fine sintered-glass disk.

Experimental Data

Measurements of flow time were made with solutions covering the concentration range 0.05 to 1.0% (grams per 100 ml. solution); and these are recorded as relative flow times. If the kinetic energy correction were really negligible then the relative flow time t_r would be equal to the relative kinematic viscosity, ν_r ; if the density of the solutions were the same as that of the solvent, then $t_r = \nu_r = \eta_r$, the relative viscosity. In many investigations density differences and kinetic energy corrections are assumed negligible (or ignored!) and measurements of relative flow time are recorded as relative viscosities. The term 'relative flow time' (11) is much less ambiguous and, for our purposes, just as useful. Since in our work the kinetic energy correction is small and the rate of change in density with concentration very small, t_r is for practical purposes a measure of η_r and $[t]$ a measure of $[\eta]$.

In work of this kind it is common practice to prepare the various solutions by successive dilution of the most concentrated solution. This is particularly true of the most dilute solutions, for if they were prepared directly slight errors in sampling or weighing would disproportionately affect the results. In order to test the various equations relating viscosity and concentration, and at the same time indicate the precision and reproducibility of the data,

25 solutions were prepared by successive dilution of five original solutions (*A*, *B*, *C*, *D*, and *E*) made up, as described above, using samples of GR-S from widely separated portions of a 7 lb. bale. In Table I, *A*-1, *A*-2, *A*-3, *A*-4, are the solutions prepared from Solution *A*, *B*-1, *B*-2, *B*-3, *B*-4 from *B*, etc. (*D*-3 and *D*-4 unfortunately never reached the viscometer!) To replace *D*-4, a solution *F*-4 was made up by successive dilution of one whose concentration was 0.4192 gm. per 100 ml. solution. The measurements on a given series were made at one time to minimize any possible effects due to ageing, incipient gel-formation, etc.

In Table I are given the measured values of *t*, the flow time, and the calculated values of $t_r^{1/n}$ for $n = 1, 3, 5, 6, 7, 8, 9, 10$, and 12. These are the data necessary for testing the Baker equation.

TABLE I
RELATIVE FLOW TIME FUNCTIONS
Viscometer A-25. Temp., $25.00 \pm 0.01^\circ \text{C}$. Solvent: technical benzene
(freed from thiophene) redistilled.
 $t_0 = 171.0 \text{ sec.}$

Soln. No.	Concentration, gm. GR-S/100 ml. soln.	t	Log t_r	t_r^1	$t_r^{1/3}$	$t_r^{1/5}$	$t_r^{1/6}$	$t_r^{1/7}$	$t_r^{1/8}$	$t_r^{1/9}$	$t_r^{1/10}$	$t_r^{1/12}$
A	1.0049	970.6	0.75405	5.6761	1.7838	1.4152	1.3356	1.2815	1.2424	1.2127	1.1896	1.1557
B	0.9004	841.5	0.69205	4.9210	1.7009	1.3753	1.3042	1.2556	1.2204	1.1937	1.1728	1.1420
C	0.8000	728.2	0.62924	4.2583	1.6209	1.3361	1.2731	1.2300	1.1986	1.1747	1.1559	1.1281
D	0.7072	633.2	0.56854	3.7031	1.5471	1.2993	1.2438	1.2056	1.1779	1.1566	1.1399	1.1153
E	0.6010	536.7	0.49673	3.1386	1.4640	1.2570	1.2100	1.1775	1.1537	1.1355	1.1212	1.1000
A-1	0.5025	455.7	0.42569	2.6650	1.3864	1.2166	1.1775	1.1503	1.1304	1.1151	1.1030	1.0851
B-1	0.4502	415.2	0.38526	2.4280	1.3441	1.1942	1.1594	1.1351	1.1173	1.1036	1.0928	1.0767
C-1	0.4000	378.2	0.34472	2.2115	1.3029	1.1720	1.1414	1.1200	1.1043	1.0922	1.0826	1.0684
D-1	0.3536	346.2	0.30634	2.0246	1.2650	1.1515	1.1248	1.1060	1.0922	1.0815	1.0731	1.0605
E-1	0.3005	314.7	0.26490	1.8403	1.2254	1.1297	1.1070	1.0910	1.0792	1.0701	1.0629	1.0521
A-2	0.2512	285.2	0.22216	1.6678	1.1861	1.1077	1.0890	1.0758	1.0660	1.0585	1.0525	1.0435
B-2	0.2251	270.5	0.19917	1.5819	1.1651	1.0960	1.0794	1.0679	1.0590	1.0523	1.0469	1.0389
C-2	0.2000	257.9	0.17845	1.5082	1.1467	1.0856	1.0709	1.0604	1.0527	1.0467	1.0419	1.0348
D-2	0.1768	245.6	0.15723	1.4363	1.1283	1.0751	1.0622	1.0531	1.0463	1.0410	1.0369	1.0306
E-2	0.1503	232.6	0.13361	1.3603	1.1080	1.0635	1.0526	1.0449	1.0392	1.0348	1.0312	1.0260
A-3	0.1256	220.8	0.11100	1.2913	1.0889	1.0524	1.0435	1.0372	1.0325	1.0288	1.0259	1.0215
B-3	0.1126	215.2	0.09984	1.2585	1.0796	1.0470	1.0390	1.0334	1.0292	1.0259	1.0232	1.0193
C-3	0.1000	209.9	0.08901	1.2275	1.0707	1.0418	1.0347	1.0297	1.0260	1.0230	1.0207	1.0172
D-3	0.0884	205.0	0.07875	1.1986	1.0623	1.0369	1.0306	1.0262	1.0229	1.0203	1.0183	1.0152
E-3	0.0751	199.9	0.06781	1.1690	1.0533	1.0317	1.0263	1.0225	1.0197	1.0175	1.0157	1.0131
A-4	0.0628	194.8	0.05659	1.1394	1.0445	1.0264	1.0220	1.0188	1.0164	1.0146	1.0131	1.0109
B-4	0.0563	192.3	0.05098	1.1248	1.0400	1.0238	1.0198	1.0170	1.0148	1.0131	1.0118	1.0099
C-4	0.0500	189.8	0.04530	1.1102	1.0355	1.0211	1.0176	1.0150	1.0131	1.0116	1.0105	1.0087
F-4	0.0262	180.4	0.02324	1.0550	1.0180	1.0108	1.0090	1.0077	1.0067	1.0060	1.0054	1.0045

Discussion of Results

(1) The Most Suitable Form of the Baker Equation

If the equation

$$t_r = \left(1 + \frac{[t]}{n} c\right)^n \quad (9) \text{ cf. } (5)$$

fits the data, then

$$t_r^{1/n} = 1 + \frac{[t]}{n} c,$$

and a plot of $t_r^{1/n}$ vs. c should give a straight line. When the data of Table I were so plotted it was found that a straight line over the widest range of concentration was obtained with $n = 7$ or 8 or 9, and that (as might be expected) there was little to choose between these values (see Fig. 1). It is, however, difficult to compare the plot on one graph as the lines all converge at the origin ($t_r^{1/n} = 1, c = 0$).

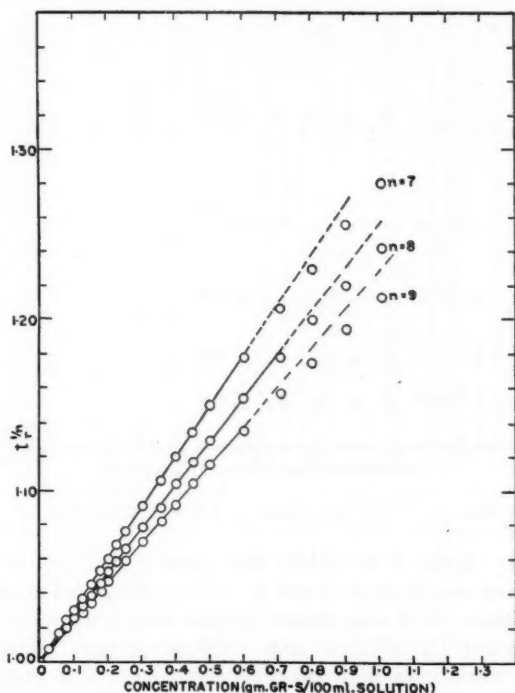


FIG. 1. $t_r^{1/n}$ vs. c , for $n = 7, 8$, and 9 .

If however, the relation between $t_r^{1/n}$ and c is linear over a range of concentrations, then the slope $\frac{d(t_r^{1/n})}{dc}$ is constant and is equal to $(t_r^{1/n} - 1)/c$ for any value of c within that range. In other words a plot of $\frac{t_r^{1/n} - 1}{c}$ vs. c is a horizontal straight line so long as the $t_r^{1/n}$ vs. c curve is linear. In Fig. 2, $\frac{t_r^{1/n} - 1}{c}$ is plotted against c for the various values of n . From this figure it is apparent that the best values of n are 7 to 9.

Since the slope of the straight line is $\frac{[t]}{n}$, the intrinsic flow time

$$[t] = \left(\frac{t_r^{1/n} - 1}{c} \right) n. \quad (10)$$

A plot of $n \left(\frac{t_r^{1/n} - 1}{c} \right)$ vs. c will therefore not only be a horizontal straight line but can be extrapolated in the simplest possible way to $c = 0$ to obtain the value of $[t]$. In Fig. 3 the curves are plotted, for $n = 7, 8$, and 9 , from the

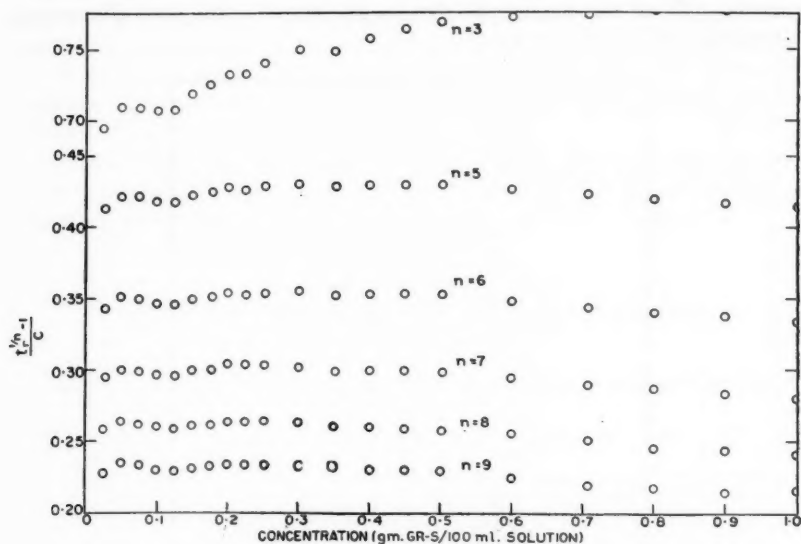


FIG. 2. $\frac{t_r^{1/n} - 1}{c}$ vs. c , for $n = 3, 5, 6, 7, 8$, and 9 .

data of Table II. Again it is evident that there is little to choose between the three, and even less between 7 and 8. Other things being equal, or very nearly so, the value $n = 8$ was chosen because this is the value found most suitable by Howlett for cellulose, and cellulose acetate, solutions and by Philippoff for a variety of high polymer solutions. The precision of our measurements scarcely justifies a selection on any other grounds; measurements of a higher order of precision (30) might make it possible to choose a value of n with greater confidence.

(2) Comparison of Plots

A plot of $n \left(\frac{t_r^{1/n} - 1}{c} \right)$ vs. c gives a value of $[t] = 2.09 \pm 0.02$ whether $n = 7, 8$, or 9 (Fig. 3). The other functions that are in common use, or that have been strongly recommended, for evaluating $[t]$ have been plotted in Figs. 4, 5, and 6, from the data of Table III.

It is evident (Fig. 4) that the inherent flow time $\frac{\ln t_r}{c}$ (11), does not give a horizontal straight line. A line can be drawn through the points that will give $[t] = 2.09$, and it is a good choice; but without this guidance a choice of the most suitable line, and particularly of the most suitable slope of the

TABLE II
CALCULATED VALUES OF $n \left(\frac{t_r^{1/n} - 1}{c} \right)$

Soln. No.	Concentration, gm. GR-S/100 ml. soln.	$n = 1$	$n = 3$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 12$
A	1.0049	4.65	2.34	2.07	2.00	1.96	1.93	1.91	1.89	1.86
B	0.9004	4.35	2.34	2.08	2.03	1.99	1.96	1.94	1.92	1.89
C	0.8000	4.07	2.33	2.10	2.05	2.01	1.99	1.97	1.95	1.92
D	0.7072	3.82	2.32	2.11	2.07	2.04	2.01	1.99	1.98	1.96
E	0.6010	3.56	2.32	2.14	2.10	2.07	2.05	2.03	2.02	1.99
A-1	0.5025	3.24	2.31	2.15	2.12	2.09	2.07	2.06	2.05	2.03
B-1	0.4502	3.17	2.29	2.15	2.12	2.10	2.08	2.07	2.06	2.04
C-1	0.4000	3.03	2.27	2.15	2.12	2.10	2.09	2.08	2.07	2.05
D-1	0.3536	2.90	2.25	2.14	2.12	2.10	2.09	2.07	2.07	2.05
E-1	0.3005	2.80	2.25	2.16	2.14	2.12	2.11	2.10	2.09	2.08
A-2	0.2512	2.66	2.22	2.14	2.13	2.11	2.10	2.10	2.09	2.07
B-2	0.2251	2.58	2.20	2.13	2.12	2.11	2.10	2.09	2.08	2.07
C-2	0.2000	2.54	2.20	2.14	2.13	2.11	2.11	2.10	2.09	2.08
D-2	0.1768	2.47	2.17	2.12	2.11	2.10	2.10	2.09	2.09	2.07
E-2	0.1503	2.39	2.16	2.11	2.10	2.09	2.09	2.08	2.07	2.07
A-3	0.1256	2.32	2.12	2.09	2.08	2.07	2.07	2.06	2.06	2.05
B-3	0.1126	2.29	2.12	2.09	2.08	2.08	2.08	2.07	2.06	2.05
C-3	0.1000	2.27	2.12	2.09	2.08	2.08	2.08	2.07	2.07	2.06
D-3	0.0884	2.25	2.11	2.09	2.08	2.08	2.07	2.07	2.07	2.06
E-3	0.0751	2.25	2.13	2.11	2.10	2.11	2.10	2.10	2.09	2.08
A-4	0.0628	2.22	2.13	2.10	2.10	2.10	2.09	2.09	2.08	2.07
B-4	0.0563	2.22	2.13	2.11	2.11	2.10	2.10	2.09	2.10	2.08
C-4	0.0500	2.20	2.13	2.11	2.11	2.10	2.10	2.09	2.10	2.08
F-4	0.0262	2.10	2.06	2.06	2.05	2.06	2.05	2.06	2.07	2.06

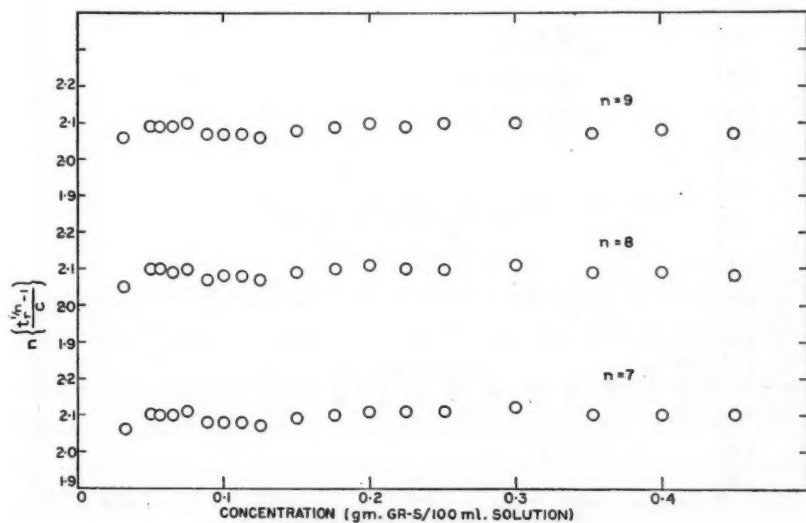


FIG. 3. $n \left(\frac{t_r^{1/n} - 1}{c} \right)$ vs. c , for $n = 7, 8$, and 9 .

TABLE III
VALUES OF VARIOUS FLOW TIME FUNCTIONS

Solution No.	Concentration, gm. GR-S/100 ml. soln.	$8\left(\frac{t_r^{1/8}-1}{c}\right)$	$\frac{t_{sp}}{c}$	t_{sp}	$\frac{\ln t_r}{c}$	$\log \frac{t_{sp}}{c}$
A	1.0049	1.93	4.65	4.68	1.73	0.6678
B	0.9004	1.96	4.36	3.92	1.77	0.6390
C	0.8000	1.99	4.07	3.26	1.81	0.6099
D	0.7072	2.01	3.82	2.70	1.85	0.5823
E	0.6010	2.05	3.56	2.14	1.90	0.5512
A-1	0.5025	2.07	3.24	1.67	1.95	0.5203
B-1	0.4502	2.08	3.17	1.43	1.97	0.5014
C-1	0.4000	2.09	3.03	1.21	1.99	0.4813
D-1	0.3536	2.09	2.90	1.03	2.00	0.4620
E-1	0.3005	2.11	2.80	0.84	2.03	0.4465
A-2	0.2512	2.10	2.66	0.67	2.04	0.4246
B-2	0.2251	2.10	2.58	0.58	2.03	0.4123
C-2	0.2000	2.11	2.54	0.51	2.05	0.4048
D-2	0.1768	2.10	2.47	0.44	2.05	0.3925
E-2	0.1503	2.09	2.39	0.36	2.05	0.3797
A-3	0.1256	2.07	2.32	0.29	2.04	0.3652
B-3	0.1126	2.08	2.29	0.26	2.04	0.3606
C-3	0.1000	2.08	2.27	0.23	2.05	0.3566
D-3	0.0884	2.07	2.25	0.20	2.05	0.3515
E-3	0.0751	2.10	2.25	0.17	2.08	0.3515
A-4	0.0628	2.09	2.22	0.14	2.08	0.3463
B-4	0.0563	2.10	2.22	0.13	2.09	0.3457
C-4	0.0500	2.10	2.20	0.11	2.09	0.3432
F-4	0.0262	2.05	2.10	0.06	2.04	0.3221

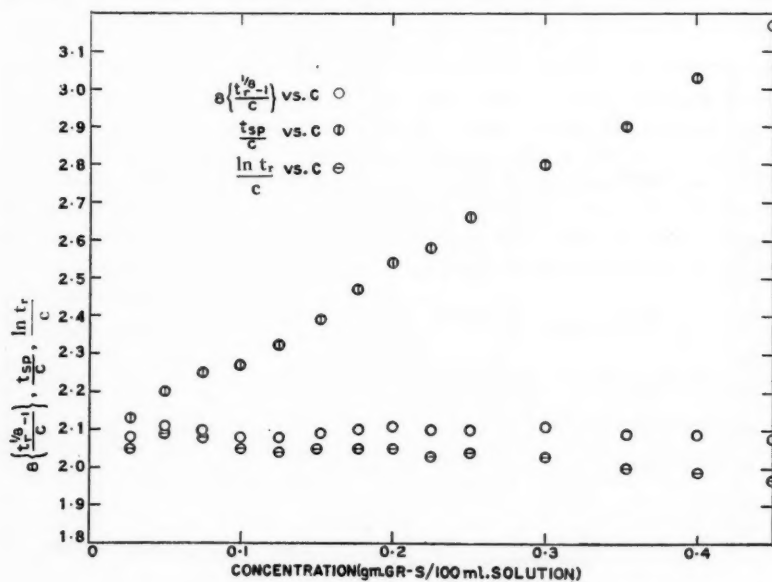


FIG. 4. Comparison of $8\left(\frac{t_r^{1/8}-1}{c}\right)$ vs. c with the two most widely used plots.

line, is difficult. The advantage of $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ vs. c is that the slope is known; the line chosen must be horizontal. (This point has been well made by Howlett *et al.*)

The reduced flow time, $\frac{t_{sp}}{c}$, has the added disadvantage that it gives a curved line. An extrapolation is not only difficult but gives most weight to the points that can least bear it, namely, those in the low concentration range

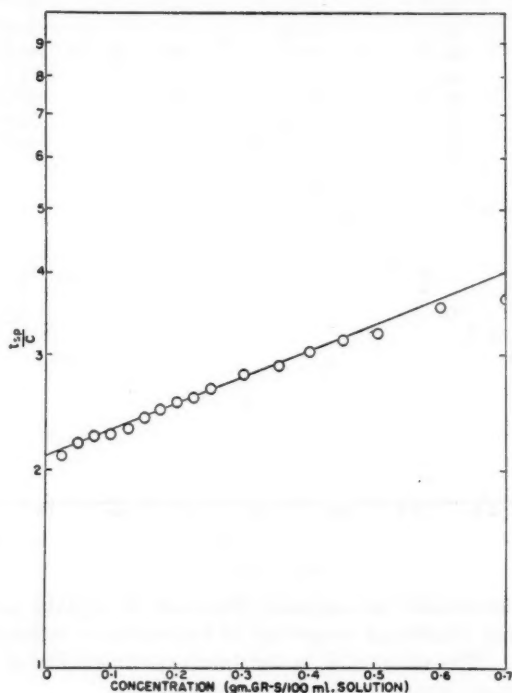


FIG. 5. $\log t_{sp}/c$ vs. c .

(*vide supra*). It is, however, easy to draw a curve that will extrapolate to 2.09. $\log \frac{t_{sp}}{c}$ gives a straight line (Fig. 5)—and one that is relatively easily selected—over the same range as $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$, and the value of $[\eta]$ obtained by extrapolation is again 2.09. This plot, although superior to those involving $\frac{\ln t_r}{c}$ and $\frac{t_{sp}}{c}$, appears to have no advantage over $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ vs. c , and has the disadvantage that determinations of t_r for at least three solutions of different concentrations would be required to fix the position of the line. (The slope is *not* independent of molecular weight. See Equations (6) and (7).)

Advantages have been claimed for the t_{sp}/c vs. t_{sp} plot, among them that it yields a straight line over a wide range and that it has a sound theoretical background (10). From Fig. 6 it is obvious that, for this system at least, it is inferior to either $\log t_{sp}/c$, c or $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$, c . And not too much should be made of the theoretical support, for in arriving at the equation

$$\eta_{sp}/c = [\eta] (1 + K' \eta_{sp}), \quad (11)$$

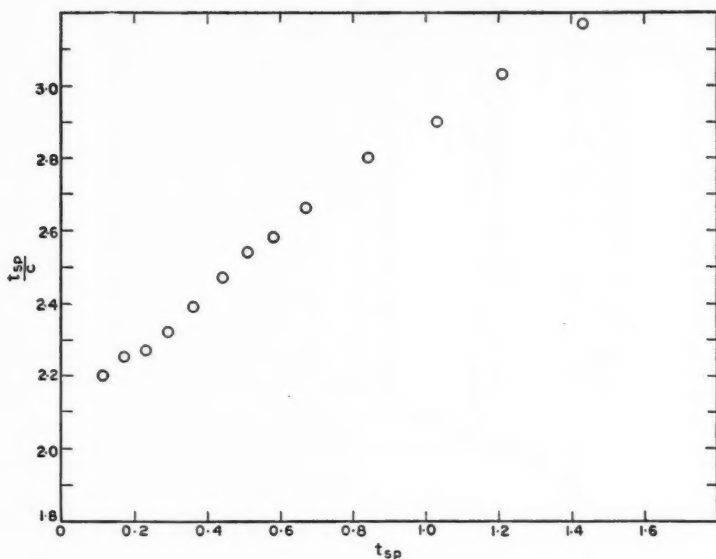


FIG. 6. t_{sp}/c vs. t_{sp} .

Huggins (21) introduced an empirical constant K' to take account of "the sizes, shapes and cohesive properties of both solvent molecules and solute submolecules". The value of K' is obtained experimentally or by calculation from the empirical constants of other equations.

We conclude, then, that, for this system at least, the most satisfactory methods of determining $[\eta]$ —and therefore $[\eta]$ —involve extrapolation of curves obtained by plotting $\frac{\ln t_r}{c}$, or $\log \frac{t_{sp}}{c}$, or $n \left(\frac{t_r^{1/n} - 1}{c} \right)$, against c ; and of these the last is the most precise. Indeed the evidence given here leads to the conclusion that it is two or three times as precise as the other two, and many other experiments in this laboratory tend to confirm it. Table IV and Fig. 7 give the results of one such experiment on another sample of plant-run GR-S. Here the intrinsic flow time is 2.20, and again the method gives a value of $[\eta]$ with a precision of $\pm 1\%$ or better. The horizontal line might be drawn through any *one* of the points to yield a value of $[\eta]$ in this range; lines drawn through the minimum two points on the $\frac{\ln t_r}{c}$, c plot give values

TABLE IV

TYPICAL VALUES OF THREE FLOW TIME FUNCTIONS FOR PLANT GR-S

(Sample received from Sarnia, July 17, 1945)

Solution No.	Concentration, gm. GR-S/100 ml. soln.	t_r	$8\left(\frac{t_r^{1/8}-1}{c}\right)$	$\frac{t_{sp}}{c}$	$\frac{\ln t_r}{c}$
1	0.3132	1.952	2.22	3.04	2.14
2	0.2513	1.704	2.19	2.80	2.12
3	0.2035	1.552	2.22	2.71	2.16
4	0.1524	1.386	2.19	2.54	2.14
5	0.1030	1.252	2.21	2.44	2.18
6	0.0805	1.189	2.18	2.35	2.15
7	0.0431	1.101	2.22	2.34	2.22
8	0.0201	1.046	2.22	2.28	2.22

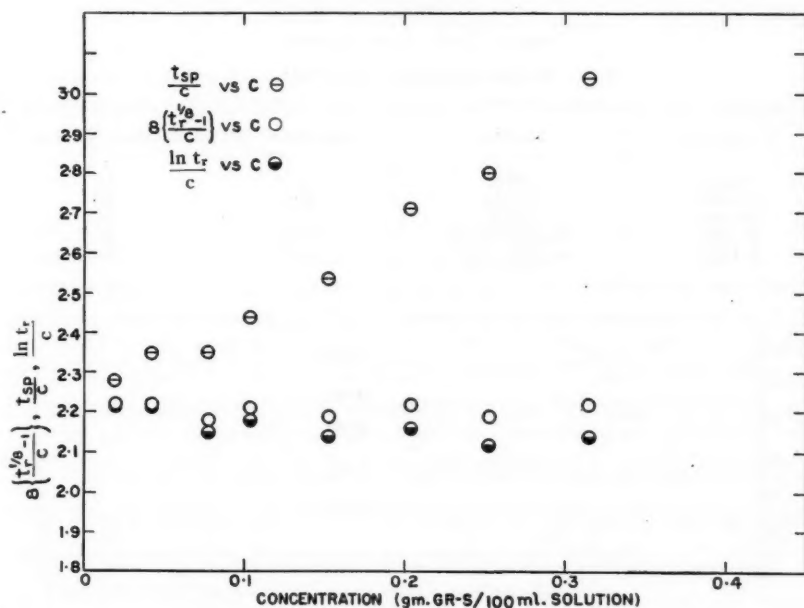


FIG. 7. Viscosity-concentration relations; second sample of GR-S.

ranging between 2.0 and 2.35, and, through three well-scattered points, values of 2.15 and 2.23!

It seems reasonable to conclude therefore that the intrinsic flow time of unfractionated GR-S in benzene may be determined most precisely by horizontal linear extrapolation of a curve relating $8\left(\frac{t_r^{1/8}-1}{c}\right)$ and c , or, what

amounts to the same thing, averaging several values of $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ with-
in the range $c = 0.10$ to 0.45 (or, better, $t_r = 1.2$ to 2.4).

(3) *General Validity of the Method for GR-S - Benzene Systems*

The method here recommended has been equally satisfactory with many samples of normal GR-S of different intrinsic viscosity, made in the plant at Sarnia at different times. To be of maximum value it should, however, be applicable to rubbers of the GR-S type polymerized under widely varying conditions: with different charge ratios of monomers, with various modifiers, to different conversions, etc. Measurements on a wide variety of such rubbers are being made, but such as have been completed suggest strongly that the method is generally applicable. For example, values of $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ for five different rubbers (see Table V) specially prepared at Sarnia for other work in this laboratory are plotted in Fig. 8.* The method seems to be as suitable for

TABLE V
SPECIAL GR-S - TYPE RUBBERS
(Prepared in Sarnia, Dec. 1945)

Charge No.	Modifier	Conversion, %	Mooney viscosity
P-443-1	DDM	73.3	45
B 1570	DDM	46.0	50
B 1569	DDM	71.6	46
B 1556	Tertiary C-14	75.5	45
B 1562	Sharples 3-B	75.2	50

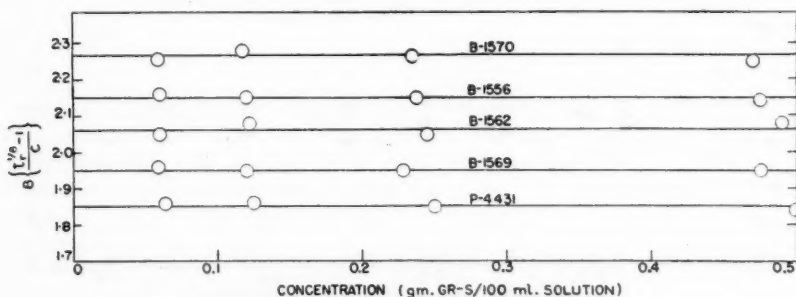


FIG. 8. Variation of $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ with c , for five special rubbers.

these as for normal GR-S rubbers. (It should be added that although the method has proved satisfactory for determining the value of the intrinsic viscosity of *whole* GR-S (in wide variety) in several solvents it has not been

* As these rubbers contained some gel, the solutions were made by static extraction in the dark in a Baker cell, and the concentration of the undiluted solution was determined by evaporation of the solvent, from an aliquot sample, at 60° to 70° C. on a hot plate and finally in a vacuum oven.

adequately tested for use with fractionated samples. Indeed there is evidence that with high or low molecular weight fractions a plot of $n \left(\frac{(\eta_r^{1/n} - 1)}{c} \right)$ against c does *not* give a horizontal line when $n = 8$; it does, however, give a straight line suitable for extrapolation, and a proper choice of n might restore the additional advantage of a zero slope.)

(4) *The Significance of n*

It has been pointed out by Huggins (21) and others, that viscosity-concentration equations containing an adjustable constant should give better agreement than inflexible equations such as those of Arrhenius or Philippoff. The value of such a constant depends on the nature of the solute and of the solvent and on the temperature, but is independent of molecular weight. Huggins showed (21) that many of these constants can be expressed in terms of the K' of Equation (2). Ewart (13, p. 211) pointed out that if the inherent viscosity is related to the concentration by the equation (27)

$$\frac{\ln \eta_r}{c} = [\eta] - \beta [\eta]^2 c, \quad (12)$$

the constant β is related to K' by the expression $\beta = 0.50 - K'$.

By expanding the modified Baker Equation (5) binomially and neglecting higher terms in c , it may be shown that

$$K' = (n - 1)/2n \\ \text{and } \beta = 1/2n$$

Ewart emphasizes the importance of determining the value of K' or β ; obviously the evaluation of n would be just as useful.

It is perhaps worth pointing out that in terms of K' or β there is very little difference between the values $n = 7$ and $n = 9$; the range $n = 8 \pm 1$ is equivalent to $K' = 0.437 \pm 0.008$ or to $\beta = 0.064 \pm 0.008$. To make it possible to make an unequivocal choice between $n = 7$ and $n = 8$, measurements would have to be precise enough to fix the $\frac{\ln \eta_r}{c}$ slope as $0.071 [t]^2$ rather than $0.062 [t]^2$. If $\frac{\ln \eta_r}{c}$ is to be independent of c , n must be infinite.

If n is a finite number, the $\frac{\ln \eta_r}{c}$, c line cannot be horizontal, and its slope will increase with increasing molecular weight of the polymer.

(5) *The One-Point Determination of Intrinsic Flow Time*

For routine use there are very obvious advantages in a method by which intrinsic viscosity may be calculated from a single measurement of flow time. (For this purpose, certainly, $[t]$ and $[\eta]$ may be regarded as equivalent (3, 36).) Any viscosity-concentration function that reduces in the limit ($c \rightarrow 0$) to $[\eta]$ and is linear up to a concentration where precise measurement is possible could in principle be adapted to such a one-point determination. Nevertheless the function that is most frequently used in this way is the inherent viscosity, for, in general, it is much less dependent on c than the other functions commonly

employed. The relative flow time is determined at a concentration such that t_r lies in the range 1.2 to 1.4 (15, 16, 17, 24), and $[\eta]$ is calculated as $\frac{\ln t_r}{c}$ (15).

It is evident, from Fig. 4 and from Table III, that the function $8 \left(\frac{t_r^{1/8} - 1}{c} \right)^*$ would be more suitable than $\frac{\ln t_r}{c}$ for this purpose. It gives a value closer to the true (extrapolated) value than does $\frac{\ln t_r}{c}$ even in the range $t_r = 1.2 - 1.4$, where the latter is most precise, and, being independent of concentration over a wide range, it can be used at concentrations where t_r is a larger and therefore more precisely measurable quantity.

The two methods were put to a practical test by having five experimenters make independent measurements and compute $[\eta]$ using the two different functions. The results are given in Table VI. They should be compared with the value, $[\eta] = 2.09 \pm 0.01$, obtained by extrapolation.

TABLE VI
ONE-POINT DETERMINATIONS OF INTRINSIC FLOW TIME

Experimenter	Date of test	Concentration, gm. GR-S/100 ml. soln.	t_0 , sec.	t , sec.	$8 \left(\frac{t_r^{1/8} - 1}{c} \right)$	$\frac{\ln t_r}{c}$
S.Z.	Feb. 27	0.2371	171.1	276.3	2.08 ₅	2.02 ₅
S.Z.	Feb. 27	0.0813*	171.1	202.1	2.07 ₀	2.04 ₅
L.M.F.	Feb. 27	0.0790*	170.8	201.0	2.08 ₆	2.06 ₁
L.M.F.	Feb. 27	0.2733	170.8	297.2	2.09 ₈	2.02 ₇
D.A.H.	Feb. 28	0.2019	171.0	257.6	2.08 ₀	2.02 ₇
D.S.	Feb. 28	0.2043	171.0	260.2	2.11 ₀	2.05 ₅
P.B.S.	Feb. 28	0.2112	171.0	263.3	2.09 ₈	2.04 ₅

The apparatus and technique used were those already described. With one exception (P.B.S., whose values of t_0 and t were averages of readings obtained with only one filling of the viscometer) the values represent the mean of measurements with more than one filling. The precision in all cases was ± 0.1 sec. Each experimenter took his sample from a different portion of the 7 lb. bale.

It is noteworthy that with the proposed method all the values lie in the range 2.09 ± 0.02 ($2.09 \pm 1\%$). On the other hand, the values of the inherent flow time, $\frac{\ln t_r}{c}$, vary as much as $3\frac{1}{2}\%$ from the 'correct' value. Even

* A function of this form, viz. $\frac{8}{c} (\sqrt[8]{\eta_r} - 1)$, has been used by Hess and Philippoff (19) and by Conrad (8).

the determinations made in the recommended range (marked *) are in error by at least $1\frac{1}{2}\%$.*

As these results were obtained by five different experimenters whose experience with this sort of measurement differed widely, and, as samples were taken at random, it seems reasonable to conclude that any well trained technician could obtain comparable results. In routine practice, therefore the intrinsic viscosity of whole GR-S may be more precisely determined as $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ than as $\frac{\ln t_r}{c}$.

It might of course be argued that $\frac{\ln t_r}{c}$ or for that matter t_{sp}/c or $\log \frac{t_{sp}}{c}$, could give equally precise values of $[\eta]$ if the slope constant β (or K' , or K) were determined once and for all for the given polymer-solvent system (as we have determined n). In each case, however, the slope term includes $[\eta]^2$ as well as the constant, so that calculation would have to be done by successive approximation. The desire to avoid such calculations doubtless accounts for the widespread preference for the use of $\frac{\ln t_r}{c}$ as an approximation of $[\eta]$.

It is evident, therefore, that $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ rather than $\frac{\ln t_r}{c}$ best combines convenience and precision for a one-point determination of intrinsic viscosity. The formula has been proved valid for a wide variety of rubbers of the GR-S type, and may be safely used with unfractionated normal GR-S. If, however, a rubber is known (or suspected) to differ markedly from normal GR-S, the formula should first be tested by determining t_r at several concentrations and plotting $8 \left(\frac{t_r^{1/8} - 1}{c} \right)$ against c .

With normal GR-S (for which $[\eta]$ is about 2) a suitable concentration is 0.25 gm. per 100 ml. solution; in general the concentration should be such that the value of t_r is between 1.4 and 2.2.

Acknowledgment

We wish to express our appreciation to the National Research Council of Canada for the Bursary granted to one of us (D. A. H.) and for financial support for the research received through the Associate Committee on Synthetic Rubber Research.

* This, of course, is what might be expected. If $n = 8$, the slope of the $\frac{\ln t_r}{c}$, c curve is $-0.06_3 [i]^2$. Assuming no error in the determination of $\frac{\ln t_r}{c}$ at $c = 0.08$ (a very brave assumption indeed!) the error in the value of $[i]$ caused by supposing $\frac{\ln t_r}{c}$ to be independent of c is $0.06_3 \times [i] \times 0.08 \times 100\%$ or, when $[i] = 2.1$, 1% . And, of course, when $c = 0.3$, where measurement is much more precise, this error is much larger, 4% .

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A NOTE ON THE VARIATION WITH TEMPERATURE OF THE INTRINSIC VISCOSITY OF GR-S IN BENZENE¹

BY T. M. ROGERS,² D. A. HENDERSON,³ AND L. H. CRAGG⁴

Abstract

The intrinsic viscosity, $[\eta]$, (as well as the intrinsic flow time, $[t]$, and the intrinsic kinematic viscosity, $[\nu]$) of normal GR-S in benzene has been shown to be independent of temperature, over the range 10° to 55° C., within the experimental precision ($\pm \frac{1}{2}\%$). In this range of temperatures, also, the functions $8 \frac{(\eta^{1/8} - 1)}{c}$ and $8 \frac{(\nu^{1/8} - 1)}{c}$ are independent of concentration (up to at least 0.3%), and may therefore be used in the one-point determination of $[\eta]$ and $[\nu]$.

Introduction

The viscosity of a solution of a high polymeric substance is very sensitive to changes in temperature; but since the viscosity of the solvent is likewise sensitive, and in the same sense, the relative viscosity of the solution (i.e., its viscosity relative to that of the solvent) is much less dependent on the temperature. With some substances, such as cellulose and its derivatives, this temperature dependence is still considerable; with others, such as natural rubber, and many synthetic polymers (11; 12, pp. 203-220; 9; 13) it is relatively small.

The results obtained by different investigators with a given polymer, such as rubber (1, 7, 8, 11, 16), are often contradictory, but the discrepancies may be attributed to the fact that measurements were made in a variety of solvents and at different concentrations (7). Such discrepancies would of course be avoided if intrinsic viscosities were determined, in one solvent. Few careful studies of the variation of intrinsic viscosity with temperature have been reported—none, so far as we are aware, for the important system GR-S—benzene. Unpublished results* indicate that the intrinsic viscosity of GR-S in benzene or in toluene varies very little with temperature and that for practical purposes it may be determined at any convenient temperature between 20° and 30° C. Because it seemed important, for both practical and theoretical (2) reasons, to know more precisely the relation between $[\eta]$ and temperature, it was decided to determine it with the precision made possible by the use of the modified Baker equation (3, 5).

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* Private communications: F. T. Wall, June 19, 1944; P. J. Flory (et al.), Sept. 13, Dec. 22, 1943.

Experimental

The apparatus and technique were essentially those described in a previous paper (5). Temperatures were maintained constant to $\pm 0.01^\circ \text{C.}$, and even at 55°C. evaporation of the solvent during measurement was quite inappreciable. In all the experiments the solvent was benzene, purified as before (5).

A preliminary investigation was made using a sample of plant GR-S (obtained from Polymer Corporation, Sarnia, July 7, 1945) and a standard Ostwald-Cannon-Fenske viscometer A.S.T.M. No. 50. Determinations of relative flow time were made at one concentration at five temperatures ranging from 15° to 55°C. Since in the function intrinsic viscosity ($[\eta] \equiv \lim_{c \rightarrow 0} \frac{\ln \eta_r}{c}$) c is the concentration in grams per 100 ml. solution (4, 10), and therefore varies with the temperature, the solutions were prepared at the temperature of measurement (see Discussion). The results, shown in Table I and Fig. 1,

TABLE I
ONE-POINT DETERMINATION OF $[\eta]$ AT DIFFERENT TEMPERATURES

Conc'n., c (gm. GR-S per 100 ml. soln. at $\theta^\circ \text{C.}$)	Temp., $\theta^\circ \text{C.}$	Rel. flow time, t_r	$[\eta]$ dl./gm.
0.1500	15.05	1.358	2.08
0.1500	25.00	1.357	2.07
0.1500	35.00	1.356	2.07
0.1500	45.00	1.355	2.07
0.1500	55.00	1.352	2.06

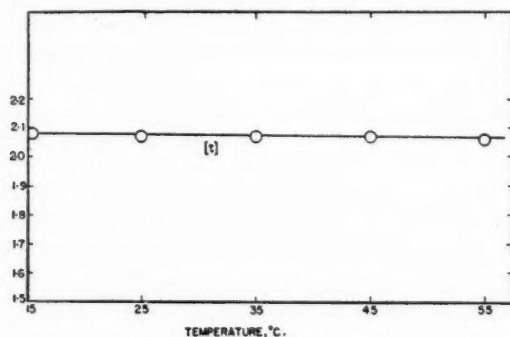


FIG. 1. Variation of intrinsic flow time with temperature.

indicate that $[\eta]$ varies linearly with temperature and is practically constant over the 40°C. range within which such measurements are usually made.

Independent measurements were made with a different sample of GR-S and a different viscometer. The GR-S came from the same bale as that used in

an earlier investigation (5); the dimensions of the viscometer have already been given in detail (5).

Two solutions of GR-S in benzene were prepared, of concentrations 0.3066 gm. per 100 ml. at 10.00° C. and 0.3010 gm. per 100 ml. at 50.00° C. These were successively diluted at the respective temperatures, giving six solutions in each series. The experimental data and the calculated values of the function $8 \frac{(t_r^{1/8} - 1)}{c}$ are given in Table II. From these, values of $[\eta]$ are readily obtained (with a precision of ± 0.01): 2.09 at 10° and 2.08 at 50° C. (see Fig. 2).

TABLE II
THE BAKER FUNCTIONS ($n = 8$) AT TWO TEMPERATURES

10.00° C.			50.00° C.		
Concentration, gm. GR-S/100 ml. soln.	$8 \frac{(t_r^{1/8} - 1)}{c}$	$8 \frac{(\nu_r^{1/8} - 1)}{c}$	Concentration, gm. GR-S/100 ml. soln.	$8 \frac{(t_r^{1/8} - 1)}{c}$	$8 \frac{(\nu_r^{1/8} - 1)}{c}$
0.3066	2.08	2.11	0.3010	2.08	2.11
0.2537	2.08	2.11	0.2500	2.07	2.10
0.2020	2.09	2.12	0.2035	2.09	2.11
0.1583	2.09	2.13	0.1550	2.08	2.10
0.1011	2.09	2.13	0.1071	2.09	2.12
0.0570	2.10	2.13	0.0559	2.09	2.12

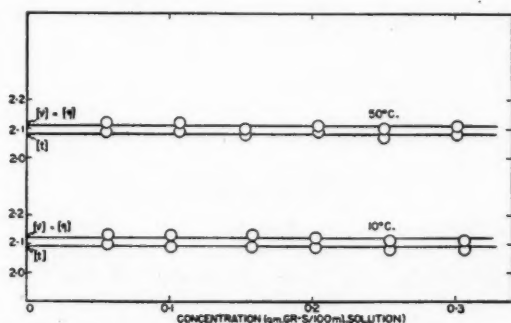


FIG. 2. Variation of $8 \frac{t_r^{1/8} - 1}{c}$ (and $8 \frac{\nu_r^{1/8} - 1}{c}$) with concentration at 10° and 50° C.

To permit calculation of $[\nu]$ and $[\eta]$ from $[\eta]$, calibration constants for the viscometer and the rate of change of the density of the solutions with concentration must be known. From measurements of the viscosity of carefully purified water, benzene, toluene, and aniline at 25° C. the constants of the equation

$$\nu = At + B/t$$

were determined for this viscometer as follows: $A = 4.122 \times 10^{-5}$, $B = -1.9 \times 10^{-2}$. By means of this equation values of relative kinematic viscosity, ν_r , and of $8 \frac{(\nu_r^{1/8} - 1)}{c}$ were calculated (Table II), and from them the values of $[\nu]$, 2.12 at 10° , and 2.11 at 50° C.

The intrinsic viscosity $[\eta]$ is theoretically not identical with $[\nu]$ (15), for if $\left(\frac{d \rho_r}{dc}\right)_{c \rightarrow 0} = \alpha$ (where ρ_r is the relative density of solution and solvent) then $[\eta] = [\nu] + \alpha^*$. The densities of three solutions of GR-S in benzene (of concentrations 0.1203, 0.2478, and 0.4018 gm. per 100 ml. solution) were carefully determined at $25.00 \pm 0.02^\circ$ C. in a modified Sprengel pycnometer. Within the experimental error the relative density was a linear function of concentration:

$$\rho_r = 1 + 9 \times 10^{-4} c.$$

Hence, at 25° C., $[\eta] = [\nu] + 0.0009$. Since the precision of our values of $[\nu]$ is no better than $\pm \frac{1}{2}\%$, it is quite safe to assume that within the experimental error $[\eta] = [\nu]$ at any temperature in the range 10° to 55° C.†

The values of $[l]$, $[\nu]$, and $[\eta]$ obtained for the GR-S - benzene system are listed in Table III.

TABLE III

TEMPERATURE DEPENDENCE OF THE INTRINSIC VISCOSITY FUNCTIONS (GR-S IN BENZENE)

Temp., °C.	$[l]$	$[\nu]$, dl./gm.	$[\eta]$
10.00 (± 0.01)	2.09 (± 0.01)	2.12 (± 0.01)	2.12 (± 0.01)
25.00	2.09 ¹	2.12	2.12
50.00	2.08	2.11	2.11

¹ Value obtained, for the same sample of GR-S, in an earlier investigation (5).

Discussion

From these results it may be concluded:

(1) That the function $8 \frac{(\nu_r^{1/8} - 1)}{c}$ is independent of c at 10° and 50° C. as well as at 25° C. (5), and may therefore be used with confidence for the one-point determination of $[l]$ at any temperature in this range.

* $\eta/\eta_0 = \nu\rho/\nu_0\rho_0$ or $\eta_r = \nu_r \rho_r$. Therefore

$$\left(\frac{d \eta_r}{dc}\right)_{c \rightarrow 0} = \left(\frac{d \nu_r}{dc}\right)_{c \rightarrow 0} + \left(\frac{d \rho_r}{dc}\right)_{c \rightarrow 0} \quad \text{or} \quad [\eta] = [\nu] + \left(\frac{d \rho_r}{dc}\right)_{c \rightarrow 0}.$$

If $\rho = \rho_0(1 + \alpha c + \beta c^2 + \gamma c^3 + \dots)$, then $\left(\frac{d \rho_r}{dc}\right)_{c \rightarrow 0} = \alpha$.

† This is in agreement with the more general observation of Wagner (14) that the error produced in the inherent viscosity (and therefore in the intrinsic viscosity) by assuming that the densities of solvent and solution are equal probably never exceeds 0.01 of a unit.

(2) That the intrinsic flow time, intrinsic kinematic viscosity, and intrinsic viscosity of GR-S in benzene are independent of temperature, within the experimental error, over the range 10° to 55° C. Any convenient temperature in this range may therefore be selected for viscosity determinations (provided of course that the temperature be the same for measurements with solvent and solution).

It should be emphasized that in this work c is the concentration in grams solute per 100 ml. solution, the volume being measured at the temperature at which viscosities are determined. As Philippoff points out (12, p. 168)

$$[\eta]_g = [\eta] \times \rho_0,$$

where ρ_0 is the density of the solvent, and $[\eta]_g$ is the function corresponding to $[\eta]$ when c is the concentration in grams solute per 100 gm. solution. In the work of Philippoff and of other investigators (particularly in Europe), it is the variation of $[\eta]_g$ with temperature that is usually determined. This has the advantage that viscosity measurements can be made on the same solution at the various temperatures; and $[\eta]$ can be calculated at each temperature from $[\eta]_g$ and ρ_0 . In this investigation, however, $[\eta]$ was determined directly, in accordance with general practice on this continent. If values of $[\eta]_g$ are desired for purposes of comparison, they may be obtained from those of $[\eta]$. Thus, at 10° C. $[\eta]_g = 1.88$, at 50° C., 1.79 hgm. per gm.* For this system the density is, with sufficient precision for the present purpose, a linear function of temperature, and $[\eta]$ is constant; therefore, in range 10° to 55° C., $[\eta]_g$ is a linear function of temperature, and

$$\frac{\Delta [\eta]_g}{\Delta t} = \frac{\Delta \rho_0}{\Delta t} [\eta] = -1.06 \times 10^{-3} [\eta].$$

The temperature independence of intrinsic viscosity of GR-S in benzene is not surprising when one considers the behaviour of related polymer-solvent systems. For example, Daneš (6) has shown that the intrinsic viscosity of styrene in benzene is almost independent of temperature over the range 15° to 65° C.; and the data of Whitby and Gallay (16) indicate that the intrinsic viscosity of natural rubber in benzene increases but very slightly with temperature.† As benzene is a 'good' solvent for these materials this behaviour is in accordance with theory (see, for example, Alfrey, Bartovics, and Mark (2)). It will be interesting to compare with that described here the behaviour of GR-S in other solvents, including 'poor' solvents and solvent-non-solvent mixtures; the necessary experiments are now in progress.

* Just as the units of $[\eta]$ are decilitres per gram (the reciprocal of grams per 100 ml.—see the letter to the Editor, *J. Colloid Sci.* 1, 465-466, 1946.), so the units of $[\eta]_g$ would be the reciprocal of grams per 100 gm., i.e., hectograms per gram.

† Values of $[\eta]$, calculated as $8 (v^{1/3} - 1)/c$ (cf. Philippoff (11)), on the assumption that $\rho_r = 1.00$, are as follows; 4.0₈ at 11°, 4.2₀ at 25°, 4.2₈ at 35°, 4.2₈ at 40°, 4.3₂ at 45°, and 4.2₈ at 50° C.

Acknowledgments

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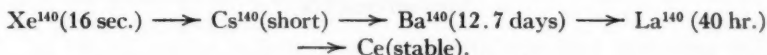
THE GROWTH OF La^{140} (40 hours) FROM Ba^{140} (12.7 days)¹

BY W. E. GRUMMITT,² J. GUÉRON,³ G. WILKINSON,⁴ AND L. YAFFE²

Abstract

The composite self-weakening relations for La^{140} and Ba^{140} have been measured. Using these data, the growth of the La^{140} daughter from the Ba^{140} parent has been studied and compared with the growth calculated from the radioactive dependence laws. It is shown that, in the comparison of the activities of different β^- emitters, there is a danger in the use of corrections obtained by extrapolations of self-weakening and external absorption data.

The barium isotope, Ba^{140} of 12.7 days half-life, was first observed in the fission products of neutron-bombarded uranium by Hahn and Strassmann (4, 5). The isotope was identified as Ba^{140} owing to the growth of a 40 hr. lanthanum daughter activity identical as regards half-life and radiation characteristics with the La^{140} isotope formed by thermal neutron capture in lanthanum. The disintegration scheme for mass 140 is



In the course of quantitative measurements on the formation of Ba^{140} in fission, it was found necessary to examine the growth of La^{140} from its parent. For the initial experiments only radium-beryllium sources were available for irradiation. In later experiments pile-irradiated material was used and the specific activity of the samples was correspondingly higher. In subsequent experiments the percentage transmission of the β^- rays through the counter windows was investigated.

Experimental

The chemical separation of barium from uranium fission products was adapted from the procedure described by Hahn and Strassmann (6). Barium, strontium, and lanthanum carriers were added, after solution of neutron-bombarded uranium oxide, UO_2 , in nitric acid, and the ice-cold solution saturated with hydrogen chloride. The precipitated barium chloride was dissolved in water. Strontium carrier and acetic acid were added, followed by 6*N* ammonium acetate solution. Barium was precipitated as chromate by dropwise addition of potassium chromate to the boiling solution.

The precipitated chromate was centrifuged, washed with hot dilute acetic acid, and dissolved in dilute hydrochloric acid. Strontium carrier was added,

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followed by acetic acid buffer solution, and barium reprecipitated as chromate. The chromate was dissolved in the minimum of dilute nitric acid, lanthanum carrier was added, and barium precipitated by addition of red fuming nitric acid to the ice-cold solution. The barium nitrate was washed with acetone, dissolved in water and reprecipitated. Two fuming nitric acid precipitations were adequate for more than 99.5% removal of lanthanum daughter activity. In some cases, barium was subsequently precipitated as sulphate.

For the high specific activity samples, a similar chemical procedure was followed. However, care was taken to keep all volumes at a minimum. The amounts of added carrier were small (1 mgm. barium) and the final nitrate precipitation was carried out in a total of 2 ml. of solution.

La^{140} was obtained from a previously separated Ba^{140} source which was in equilibrium with its daughter activity. The barium nitrate was dissolved in water, lanthanum carrier added, and lanthanum hydroxide precipitated. The hydroxide was dissolved, barium carrier added, and the precipitation repeated several times. Lanthanum was finally precipitated by hydrofluoric acid.

Measurements

The procedure used was similar to that described previously (1, 3). In order to correct for the self-weakening of the β^- rays, the activities of samples of increasing mass thickness were measured and an extrapolation was made to zero mass thickness. Six samples of varying weights were spread evenly with the aid of acetone, on circular aluminium trays of area 7.1 cm^2 . These were counted in rotation on three β^- particle counters of the end-on type with mica windows of area 7.1 cm^2 , and mass thickness $4.5 \text{ mgm. per cm}^2$. The air gap between sample and window was equivalent to a mass of 1 mgm. per cm^2 .

In view of the comparatively rapid growth of the 40 hr. lanthanum from the 12.7 day parent, it is impossible to measure directly the β^- ray self-weakening of the latter. The self-weakening of the combined barium and lanthanum activities was therefore measured at frequent intervals, starting immediately after chemical separation of barium until transient equilibrium between parent and daughter had been reached.

In the later experiments β^- samples of high specific activity (mass less than 1 microgram) were counted on an aluminium tray and on a thin mica source holder. The mica holder was constructed in such a manner as to reduce scattering of the β^- rays from the source holder into the counter. These samples were also counted using $200 \text{ mgm. per cm}^2$ aluminium as a backing material.

The activity at zero time, i.e., the time of final separation of barium from its lanthanum daughter, was obtained through a short extrapolation over the first two hours, when one can safely assume the growth of La^{140} to be a linear function of time. It is to be noted that the experimental La/Ba activity ratio depends critically on this zero value.

The external absorption of the β^- rays of the Ba^{140} and La^{140} was measured by interposing aluminium screens of varying mass thickness between the sample and counter window. From a semilogarithmic plot of these data, $\epsilon_{1/2}$, the external absorption half-thickness was found. An extrapolation of the above line to zero mass thickness was used to obtain a correction for the absorption of β^- rays in the window.

Owing to anomalies observed, further experiments on the transmission of β^- rays were performed, and for this purpose a thin-window counter was constructed. This consisted of a vacuum desiccator containing an end-on counter from which the 4.5 mgm. per cm^2 duraluminium window had been removed and replaced by a 0.2 mgm. per cm^2 silver leaf window. High tension leads were brought in through holes drilled in the desiccator sides. The sample was placed 1 cm. below the window as before. Provision was made for moving an absorber into position between the sample and counter by means of a magnet.

In operation, the sample was placed in position and the desiccator was evacuated, simultaneously evacuating the unsealed counter. The whole assembly was then filled with ethanol and argon to pressures of 0.5 and 9.5 cm. of mercury respectively.

In addition to the above, some measurements were performed with no window in the counter. No spurious effects were observed in either case.

Results

(a) Low Specific Activity Samples

In Table I, Column 2, is given the composite self-weakening half-thickness $\eta_{1/2}$ at various times. In Fig. 1, $\eta_{1/2}$ is plotted as a function of the percentage of lanthanum counts present (see below) in the total activity. The composite curve was found to follow, at all times, the logarithmic law reported earlier (1) in the case of isolated activities.* The experimental results thus obtained give, by extrapolation, the self-weakening half-thickness of both the 12.7 day Ba^{140} and the 40 hr. La^{140} . The extrapolated value of $\eta_{1/2}$ for La^{140} in barium sulphate substrate, 165 mgm. per cm^2 , agrees well with the value measured directly, 157 mgm. per cm^2 for La^{140} in lanthanum fluoride substrate. The value for Ba^{140} in barium sulphate is then estimated to be 92.5 mgm. per cm^2 .

The counts of Ba^{140} at zero time, and the composite count at various times were corrected to zero thickness of sample by use of the self-weakening data. To obtain Ba and La β^- activities, a correction was applied for absorption in the counter window, using the measured values $\epsilon_{1/2} = 41$ mgm. per cm^2 for Ba^{140} and 76 mgm. per cm^2 for La^{140} . The thinnest absorber used was 3 mgm. per cm^2 aluminium.

* It is obvious that if both radiations in a given sample obey the self-weakening relations (3) $\log \frac{N_0}{N} = \delta W$ and $\log \frac{M_0}{M} = \psi W$, the composite radiation cannot obey a logarithmic weakening law. However in the present case at least, when the self-weakening coefficients δ and ψ are not widely different, the logarithmic law is followed within the limits of experimental error.

The ratio of $(\text{La}^{140} + \text{Ba}^{140})_t$ activity at various times, t , to the Ba^{140} activity at zero time for a thick sample, corrected as above, is plotted in Fig. 2 as a function of time.

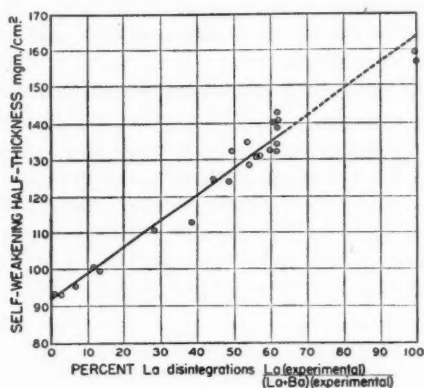


FIG. 1. Composite $(\text{Ba}^{140} + \text{La}^{140})$ β^- ray self-weakening half-thickness vs. percentage La^{140} disintegrations.

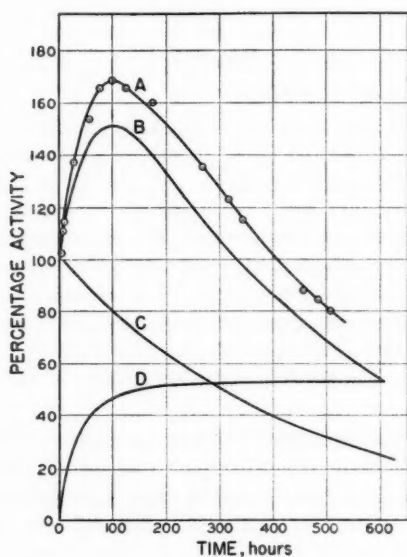


FIG. 2. Experimental and theoretical growth and decay curves for Ba^{140} and La^{140} β^- activity.

A — % $\left\{ \frac{(\text{La} + \text{Ba})_t}{(\text{Ba})_0} \right\}$ Experimental Thick sample

B — % $\left\{ \frac{(\text{La} + \text{Ba})_t}{(\text{Ba})_0} \right\}$ Theoretical

C — % $\left\{ \frac{\text{Ba}_t}{\text{Ba}_0} \right\}$ Theoretical

D — % $\left\{ \left(\frac{\text{La}}{\text{La} + \text{Ba}} \right)_t \right\}$ Theoretical

TABLE I
COMPOSITE SELF-WEAKENING AND Ba - La GROWTH DATA

Time, hr.	$\eta_{1/2}$ composite self- weakening half- thickness	Window correction applied from external absorption data				Window correction applied from 'windowless' counter experiments	
		$\frac{(\text{Ba} + \text{La})_t}{(\text{Ba})_0}$		α		Thin sample	
		Thick sample	Thin sample	Thick sample	Thin sample	$\frac{(\text{Ba} + \text{La})_t}{(\text{Ba})_0}$	α
0	93.9	100					
1.41	92.8	—					
1.67	93.8	102.68					
3.33	93.9	108.94					
5.00	95.4	111.43		1.38			
6.50	99.3	—					
6.67	100.6	114.31		1.33			
18.00	113.3	—					
24.37	110.6	137.66		1.26			
24.80	—	—	132.5		1.13	127.75	0.98
28.25	112.7	—					
45.00	119.7	—					
48.60	—	—	149.5		1.13	141.1	0.97
49.50	124.6	—					
53.40	124.8	153.82		1.17			
72.08	132.3	165.82		1.25			
72.30	—	—	156.0		1.13	146.6	0.97
76.50	124.6	—					
90.00	131.8	—					
96.50	128.2	—					
97.23	144.9	168.53		1.25			
121.23	140.8	—					
148.30	131.8	—					
170.00	—	—	148.9		1.13	137.4	0.97
173.15	142.4	160.16		1.30			
220.00	132.3	—					
264.55	140.8	135.23		1.32			
317.75	134.4	123.20		1.37			
341.12	139.4	115.15		1.33			
457.17	139.1	87.97		1.29			
480.27	139.2	84.99		1.33			
504.98	143.0	80.70		1.35			
				Average = 1.30	Average = 1.13		Average = 0.97

The growth curve for the gross activity, calculated by the theory of successive radioactive decays (assuming one electron per disintegration for both β^- emitters) is given in Fig. 2, for comparison with the experimental curve, together with the calculated curves for Ba^{140} and $\frac{\text{La}^{140}}{(\text{La}^{140} + \text{Ba}^{140})}$.

The measured values of the activity ratio $\frac{(\text{Ba}^{140} + \text{La}^{140})_t}{(\text{Ba}^{140})_0}$ are given in Table I, for thick and thin samples, together with values of α , where α is the ratio of the measured lanthanum activity to the lanthanum activity calculated from the initial barium activity stated above.

The results of Fig. 2 and Table I show that, after application of the above corrections for absorption of β^- rays, the measured growth of La^{140} from its parent in a thick source appears to be in excess of the theoretical value by the factor $\alpha = 1.30$. The experimental transient equilibrium activity ratio $\frac{\text{La}^{140}}{\text{Ba}^{140}} = 1.47$, whilst the calculated value = 1.16.

(b) *High Specific Activity Samples*

The growth of La was observed in two very thin Ba samples (about $1\mu\text{gm. per cm.}^2$) with and without backing material. Corrections were applied as previously, with the exception that a self-weakening correction was not necessary in this case. In Table I, values of α for the experiments with backing material are given. With no backing material results for α are on the average about 5% lower.

(c) *Absorption of β^- rays in the Counter Windows*

It was found that when a 5 mgm. per cm.^2 absorber was interposed between the very thin Ba^{140} sample and the thin window counter, the count was reduced to 80.5% of its former value. The result was similar when the thin window was removed. This is in contrast to an assumed value of 92% obtained by extrapolation of the external absorption, assuming, as usual, a logarithmic law, with the half-thickness of 41 mgm. per cm.^2 as quoted above. In the case of the La β^- rays the absorption by the window was found to be substantially that predicted by the extrapolation, using the experimental half-thickness of 76 mgm. per cm.^2 .

Discussion

From the results in Fig. 2 and Table I the measured growth of La^{140} from its parent is apparently in excess of the theoretical value by the factor α when window corrections are made by the usual method. The experimental transient equilibrium activity ratio $\frac{\text{La}^{140}}{\text{Ba}^{140}}$ is considerably greater than the calculated value of 1.16.

Two interpretations of this observation might be proposed.

- (1) That Ba^{140} emits one electron per disintegration to give its daughter La^{140} , which then emits 1.3 electrons per disintegration. This appears unlikely in view of β^- and γ -ray spectrometer measurements on La^{140} (2).
- (2) That Ba^{140} gives only $\frac{1}{1.3}$ electrons observable in the counting arrangement used.

This second and more likely possibility would require that part of the Ba^{140} disintegrations proceed through a soft β^- particle emission. L. G. Elliott (2) has studied Ba^{140} with a β^- ray spectrometer and has shown β^- rays of maximum energy 1.03, 0.500, and 0.34 Mev., occurring respectively in 50, 25, and 25% of the disintegrations.

The predicted transmission of these electrons, based on a maximum energy - half-thickness relation for single energy β^- emitters, is 81% through a 5 mgm.

per cm^2 window, while the observed value is 80.5%. The relation obtained using aluminium absorbers in the present geometry is similar to that given by M. Perey (7). The above values are in contrast with a predicted transmission of 92% obtained from the usual extrapolation of external absorption data.

The discrepancies in α between the thick and thin samples indicate that an error is similarly introduced by the self-weakening corrections. A deviation from linearity over the initial portion of the logarithmic self-weakening relations would not have been noticed in the present measurements because (for intensity reasons) the thinnest sample measured had already a mass thickness of 20 mgm. per cm^2 .

These observations show that in comparing the activities of different β^- emitters, there is a danger in the use of corrections obtained by extrapolation of self-weakening and external absorption data. Particularly in the case of emitters with complex spectra it is essential to use the thinnest possible samples both in actual measurements and in establishing the preliminary correction curves.

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THE FISSION YIELDS OF Ba^{139} AND Ba^{140} IN NEUTRON FISSION OF U^{235} AND U^{238}

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Abstract

The fission yields for Ba^{139} and Ba^{140} for thermal neutron fission of U^{235} and fast fission of U^{238} have been measured using naturally occurring uranium. This was accomplished by comparing the barium fission product activities with the U^{239} formed in radiative capture. With these data the fission yields were calculated from known values of the cross-sections for thermal fission and capture in uranium and were found to be 6.1% and 5.6% for Ba^{139} and Ba^{140} , respectively, for thermal fission and 5.1% and 4.2% for Ba^{139} and Ba^{140} , respectively, for fast fission. The contribution of resonance fission to the thermal neutron effect has been shown to be less than 5% in the irradiation arrangement used.

Introduction

Anderson, Fermi, and Grosse (1) introduced the concept of fission yields in the formation of fission products from uranium. The fission yield may be defined as the probability of a given isotope's being formed in fission.

$$\text{Fission yield} = \frac{\text{Number of fissions giving rise to the isotope}}{\text{Total number of fissions}}$$

A determination of the fission yield of a given isotope requires the following data:

- (a) The number of fissions occurring in a sample per unit time;
- (b) The disintegration rate of the particular isotope in the sample at a steady state. This condition is usually referred to as 'saturation of bombardment'.

The direct measurement of the number of U^{235} thermal neutron fissions occurring in a uranium sample may be avoided if natural uranium is bombarded with thermal neutrons. In this case U^{238} undergoes radiative capture to form U^{239} (23.5 min.) whilst U^{235} undergoes thermal neutron fission. The β^- activities produced both by capture and by fission in natural uranium in thermal neutron bombardment are proportional to the respective cross-sections for these processes. Thus

$$\frac{\beta^- \text{ activity of } \text{U}^{239} \text{ at saturation of bombardment}}{\beta^- \text{ activity of fission isotope at saturation of bombardment}} = \frac{\sigma_c}{Y_f \cdot \sigma_f},$$

where σ_c and σ_f are the respective capture and fission cross-sections for

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thermal neutrons in natural uranium and Y_f is the fission yield of the isotope studied.

The fission yields of Ba^{139} (86 min.) and Ba^{140} (12.7 days) produced by thermal neutron reaction with the U^{235} component of natural uranium have been measured; using additional data, yields for fast neutron fission in U^{238} have been calculated.

Experimental

The data required were the β^- activities of U^{239} , Ba^{139} , and Ba^{140} . These activities were measured after chemical separation from bombarded uranium using the usual radiochemical technique of carriers. Thermal neutron values were obtained by difference between the activities formed in the irradiation of samples in aluminium and cadmium vessels.

(i) Bombardments

The aluminium bombardment vessel consisted of two concentric cylinders with a bottom on the outer compartment. The vessel was 12 cm. high and the diameters of inner and outer tubes were 2.5 and 4 cm. respectively. An identical cadmium vessel was provided with cadmium caps for both the inner and outer tubes. The annular space was filled with about 200 gm. uranium oxide, U_3O_8 . Five curies of mixed radium-beryllium neutron sources were placed in the centre compartment, and the whole set in a paraffin block. The following irradiations were made:

- (a) Aluminium vessel in paraffin,
- (b) Cadmium vessel in paraffin,
- (c) Cadmium vessel in air as far away as possible from hydrogenous material.

Irradiations of about two hours were made for the study of Ba^{139} , whilst for Ba^{140} , the irradiation time was several weeks.

(ii) Chemical Procedures

Before bombardment, the uranium was freed from most of the UX(Th^{234}) by ether extraction of a saturated solution of uranyl nitrate. The ether solution was washed with a small quantity of water, then water extracted. This extract was evaporated and ignited to uranium oxide, U_3O_8 .

After bombardment, the oxide was dissolved in concentrated nitric acid (1 ml. per gm. U_3O_8). From the solution of total volume about 200 ml., a small sample was taken for measurement of the U^{239} activity.

- (a) *U^{239} purification.*—The uranium was precipitated from the uranyl nitrate solution as sodium uranyl acetate by the procedure given previously (4). After short irradiations one precipitation reduced sufficiently the UX and fission product contamination. For long bombardments, two precipitations were required.
- (b) *Barium purification.*—The separation of barium from uranium and other fission product activities has been described previously (7). Barium was precipitated finally as sulphate and was washed first with water, then with acetone.

(iii) *Measurements*

The β -particle counters were of the end-on type, with windows of area 7.1 cm.² and mass thickness 4.5 mgm. per cm.² All samples were of a mass thickness between 30 and 100 mgm. per cm.² and were spread evenly on circular aluminium trays of area 7.1 cm.² They were counted under reproducible conditions using a uranium reference.

The measurement of U²³⁹ activities has been described previously (4). The activity of Ba¹³⁹ was followed for about two half-lives (~ 130 min.), beginning immediately after the final separation. The long lived Ba¹⁴⁰ + La¹⁴⁰ background was obtained by measurement of the samples 24 hr. later, after complete decay of the 86 min. Ba¹³⁹ activity. Decay of the 12.7 day barium, and growth of its 40 hr. lanthanum daughter have to be considered not only for the assessment of the 12.7 day barium activity, but also as a correction to be applied to the measured decay of the 86 min. activity.

(iv) *Calculations*

Let N_2 be the measured count of (Ba¹⁴⁰ + La¹⁴⁰) at time t_2 , where t_2 is long enough to allow complete decay of Ba¹³⁹ and is measured from the end of the irradiation. Similarly t_1 is the time at which the composite (Ba¹³⁹ + Ba¹⁴⁰ + La¹⁴⁰) activity is measured ($t_1 \approx$ four hours).

Let a_1 and a_2 be the self-weakening corrections for (Ba¹⁴⁰ + La¹⁴⁰) at times t_1 and t_2 respectively. The measurement of self-weakening has been given previously (3, 6, 7). If r_1 is the quantity $\frac{(\text{Ba}^{140} + \text{La}^{140})}{\text{Ba}_{t_p}^{140}}$ at time t_1 , and r_2 is the corresponding value at time t_2 , then $\frac{N_2 a_2 r_1}{a_1 r_2}$ gives the actual number of counts due to (Ba¹⁴⁰ + La¹⁴⁰) in the sample at time t_1 . Ba¹⁴⁰ _{t_p} is the Ba¹⁴⁰ activity at the time of precipitation of barium (t_p).

If now N_0 is the number of counts of Ba¹³⁹ obtained by difference and corrected for decay to the end of irradiation (t_0), the fully corrected number of counts Ba¹³⁹ per gram U₃O₈ is then

$$N_{\text{Ba}^{139}} = N_0 \cdot a \cdot b \cdot \frac{0.893 W_c}{W_s} \cdot \frac{1}{W} \cdot \frac{1}{S},$$

where a = self-weakening correction for Ba¹³⁹ in BaSO₄,

b = correction for absorption of rays of Ba¹³⁹ in counter window and air gap,

W_s = weight of measured barium sulphate sample,

$0.893 W_c$ = weight of barium nitrate carrier used, expressed as barium sulphate,

W = total weight of uranium oxide,

S = fraction of saturation activity of Ba¹³⁹ reached during the irradiation.

Similarly, the fully corrected counts per gram U₃O₈ of Ba¹⁴⁰ is

$$N_{\text{Ba}^{140}} = \frac{N_2}{r_2} \cdot a_2 \cdot d \cdot b \cdot \frac{0.893 W_c}{W_s} \cdot \frac{1}{W} \cdot \frac{1}{S},$$

where d = correction for the β^- decay of Ba^{140} from the end of irradiation to the time t_p ,

b = correction for the absorption of Ba^{140} β^- rays in the counter,

$N_2, a_2, r_2, W_s, W_c, W$, and S have the same significance as above.

Results

For each bombardment, the fully corrected β^- counts of Ba^{140} , Ba^{139} , and U^{239} were calculated. These were averaged and are given in Table I, as counts per gram U_3O_8 bombarded. Thermal neutron activities were obtained by subtraction of the respective activities obtained from bombardments in aluminium and cadmium. In Table II are given the ratios for thermal and fast neutron fission of $\text{Ba}^{139}/\text{Ba}^{140}$, and the ratios of the U^{239} to barium activities at saturation of bombardment.

TABLE I
ACTIVITY GIVEN AS COUNTS PER GRAM U_3O_8 (AVERAGE OF FOUR EXPERIMENTS)

Experiment	Ba^{139}	Ba^{140}	U^{239}
Al in paraffin	407	274	4861
Cd in paraffin	121	77	1766
Cd difference	286	197	3095
Cd in air	113	72	295

TABLE II
ACTIVITY RATIOS AND FISSION YIELDS

	Thermal neutron fission	Fast neutron fission
$\text{Ba}^{139}/\text{Ba}^{140}$	1.45 ± 0.10	1.57 ± 0.10
$\text{U}^{239}/\text{Ba}^{139}$	10.8 ± 0.7	
$\text{U}^{239}/\text{Ba}^{140}$	15.7 ± 0.8	
Fission yield Ba^{139}	6.1×10^{-2}	5.1×10^{-2}
Apparent fission yield Ba^{140}	4.3×10^{-2}	3.2×10^{-2}

Fission Yields of Ba^{139} and Ba^{140}

The ratio $\frac{\sigma_c}{\sigma_f}$ is obtained from published values of σ_{abs} (2) and σ_f (8) through the relation $\frac{\sigma_{abs} - \sigma_f}{\sigma_f} = \frac{\sigma_c}{\sigma_f}$. Values given are $\sigma_{abs} = 5 \times 10^{-24} \text{ cm}^2$, $\sigma_f = 3 \times 10^{-24} \text{ cm}^2$ and therefore $\frac{\sigma_c}{\sigma_f} = \frac{2}{3}$. From these the fission yields of Ba^{139} and Ba^{140} can be calculated from the expressions given in the introduction.

It should be noted that, using this method, knowledge of the absolute values of σ_c and σ_f is not necessary, since only their ratio is involved. Any change in published value of the ratio $\frac{\sigma_c}{\sigma_f}$ will alter the fission yield values by the same factor.

- (a) The experimentally determined yields for thermal neutron fission of U^{235} are given in Table II. The early paper of Anderson, Fermi, and Grosse gave values of 6.4×10^{-2} and 8.4×10^{-2} for Ba^{139} and Ba^{140} respectively.
- (b) Broda, Kowarski, and West (5) studied the relation between Ba^{139} formed in fission, and the actual fission counting rate. A value of 0.84 ± 0.03 was obtained for the ratio of the amount of Ba^{139} produced per fission of U^{235} , to the amount of Ba^{139} produced per fission of U^{238} . Using this value, the fission yield for Ba^{139} and the apparent yield for Ba^{140} formed in fast fission of U^{238} can be calculated. The values are

$$Ba^{139}, \quad Y_f^1 = 0.84 \times 6.1 \times 10^{-2} = 5.1 \times 10^{-2},$$

$$Ba^{140}, \quad Y_f^1 = \frac{5.1 \times 10^{-2}}{1.57} = 3.2 \times 10^{-2}.$$

Discussion

In a previous paper (7) the authors discussed the abnormal growth of La^{140} from Ba^{140} and showed that $\frac{La \text{ experimental}}{La \text{ theoretical}} = 1.3$ owing to the existence in the Ba^{140} radiation of soft electrons which escape detection in the counting arrangement used. Thus the fission yield for this isotope and also for its daughter La^{140} is $1.3 \times 4.3 \times 10^{-2} = 5.6 \times 10^{-2}$ for thermal neutron fission, and 4.2×10^{-2} for fast neutron fission.

The 12.7 day barium can be used as a reference for determinations of fission yields of other fission isotopes by activity comparison methods, i.e., by comparison of Ba^{140} and other separated fission product activities produced in the same sample by neutron bombardment. It is to be noted, however, that if activity comparisons are made under the same experimental conditions as are used here in the measurement of the fission yield for Ba^{140} , the apparent fission yield of 4.3×10^{-2} must be used as a reference, and not the value for mass 140 of 5.6×10^{-2} .

Contribution of Resonance Fission

A maximum value for the amount of Ba^{139} and Ba^{140} produced by a resonance neutron fission process can be deduced. This is based on the comparison of irradiations in the cadmium vessel, with and without surrounding paraffin. In the first case:

- (a) Barium activity produced in fission of uranium under cadmium with paraffin present,

F = activity due to fast neutrons,

r = activity due to resonance neutrons,

n_1 = total activity of barium.

$$F + r = n_1. \quad (1)$$

In the second case:

(b) Barium activity produced in fission of uranium under cadmium with hydrogenous material removed,

F^1 = activity due to fast neutrons,

$\frac{r}{\alpha}$ = activity due to resonance neutrons,

n_2 = total activity of barium.

$$F^1 + \frac{r}{\alpha} = n_2 \quad (2)$$

$F - F^1 = \phi$, where ϕ is always positive but small, because in the experimental arrangement used, it is unlikely that many neutrons are reflected back into the sample with energy above the fast neutron fission threshold. U^{239} activity can be used as a measure of the extent to which resonance neutrons are reduced by removal of paraffin, neglecting fast neutron capture. Although this procedure is far from being strictly valid, an error in α , as determined by this means, will not affect the order of magnitude of the results.

The irradiation under cadmium (Table I) gives the result,

$$\frac{U^{239} \text{ activity with paraffin}}{U^{239} \text{ activity without paraffin}} = 6 \approx \alpha$$

From the above definitions,

$$\begin{aligned} n_1 - n_2 - \phi &= (F + r) - \left(F^1 + \frac{r}{\alpha}\right) - (F - F^1) \\ &= r - \frac{r}{\alpha} \\ &= 0.84r, \end{aligned}$$

$$\text{whence } \frac{r}{n_1} = \frac{(n_1 - n_2) - \phi}{0.84 n_1} = \frac{0.07 - \phi/n_1}{0.84} = 0.1.$$

Referring to the activity due to thermal neutron fission ($\sim 2n_1$), a maximum value of 0.05 is obtained for the ratio. This value is quite similar to the epicadmium $\frac{1}{v}$ 'tail' of thermal neutron detectors such as boron trifluoride chambers and manganese and dysprosium in a geometry comparable to the one used here. Under the experimental conditions used, therefore, resonance fission cannot contribute more than 5% of the thermal fission observed.

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FISSION YIELDS OF MASSES 131, 132, 134, AND 136 FORMED IN NEUTRON FISSION OF URANIUM¹

BY L. YAFFE² AND C. E. MACKINTOSH³

Abstract

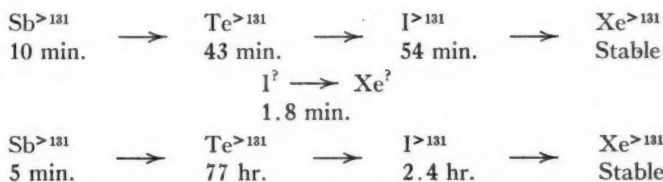
The ratio of I^{131} (8.0 days) to Ba^{140} has been determined in neutron fission of uranium and the fission yield of the former calculated to be 2.23×10^{-2} from the previously reported value for Ba^{140} . This in turn permits the estimation of fission yields for the 132, 134, and 136 fission chains, the relative abundance of which, together with that of 131, has been obtained by Thode. The ratio of 54 min. I to Ba^{139} has been determined. Using the previously reported value for the fission yield of Ba^{139} , that for the iodine was found to be 5.75×10^{-2} . A mass of 134 is assigned to the 54 min. I on the basis of Thode's data.

Introduction

In an early paper, Anderson, Fermi, and Grosse (1) introduced the concept of the fission yield of a mass chain, this being the fraction of fissions occurring in such a manner as to form that chain. It should be pointed out that in the determination of fission yields, the stable member of the chain will provide the most accurate results, since fission may occur in such a manner that the chain is entered at any point. Amongst others they determined the fission yields for the mass chain 131 produced in thermal fission. They also determined the yields for the unidentified mass chains which contained the 2.4 hr. and 54 min. iodine terms.

Broda (2) has separated I^{131} and I^{133} from the fast neutron fission products of both uranium and thorium. He determined the half-lives of these two isotopes as well as their β^- ray absorption.

There are several unidentified mass chains ending in stable Xe as reported by Seaborg (5):



The relative quantities of the stable xenon isotopes of masses 131, 132, 134, and 136 formed in fission have been determined with high accuracy by Thode and Graham (6) in a mass spectrographic study. The Xe was extracted from

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uranium that had been exposed to a high intensity of both fast and slow neutrons.

In the present paper we report the fission yield of the 8.0 day I^{131} . From this, yields can be assigned to the 132, 134, and 136 chains using the relative values obtained by Thode, assuming that no appreciable amount of Xe^{131} is formed directly in fission.

The fission yield of the 54 min. I has also been determined by comparison with that of Ba^{139} , the value for which has been previously reported (4). This, by comparison with Thode's relative values, leads us to propose a mass of 134 for the first unidentified chain above.

Experimental

(a) I^{131}

Several hundred grams of uranium oxide (UO_3) was irradiated in paraffin blocks with neutrons from a Ra-Be source for about 10 days in both aluminium and cadmium containers, as previously described (4). The source strength was kept constant for each set of experiments, but varied from 4 to 6 gm. radium from set to set.

The irradiated uranium oxide was well mixed and divided into two equal parts. Ba^{140} was extracted from one of these using the method previously described (3), and left to decay for 24 hr. to eliminate Ba^{139} , appropriate corrections being made for the growth of La^{140} .

From the second portion iodine was extracted as follows.

To the uranium oxide was added 100 mgm. potassium iodide as carrier. The mixture was then dissolved under reflux in sulphuric acid into which sulphur dioxide was bubbled constantly. After dissolution and cooling, the iodine was liberated with acidified sodium nitrite solution and extracted with carbon tetrachloride. The iodine solution in carbon tetrachloride was shaken with bromine water, and then with sodium nitrite solution to ensure against any loss of iodine. This operation was found necessary to remove traces of active bromine and was repeated three times, using fresh bromine water each time. The iodine solution was then reduced with sulphur dioxide water, reoxidized with sodium nitrite, reduced again, and copper iodide precipitated in presence of excess sulphur dioxide. The precipitate was washed with sulphur dioxide water and acetone, and then counted on paraffin-coated copper trays, using 'end-on counters'. The mica windows were 7.1 cm.² in area and of mass thickness 4.5 mgm. per cm.² The extraction yield was usually 75 to 80%.

The self-weakening and external absorption determinations were carried out on samples prepared in the same way. These data are given in Table I.

(b) 54 Min. Iodine

The samples were irradiated in paraffin as in the case of I^{131} , but for 20 min. only. In addition some samples were also irradiated in graphite, using In to monitor the (X, n) source.

TABLE I
SELF-WEAKENING AND EXTERNAL ABSORPTION IN I FOR I^{131} AND
I (54 min.) IN COPPER IODIDE SUBSTRATE

Isotope	I^{131}	I (54 min.)
Self-weakening half-thickness, $\eta_{1/2}$, mgm. per cm. ²	56 ± 6	151 ± 8
External absorption half-thickness, $\epsilon_{1/2}$, mgm. per cm. ²	22 ± 2	98 ± 4

¹ This is one of the few instances in which the ratio $\frac{\eta_{1/2}}{\epsilon_{1/2}}$ is very different from 2.2. These values were checked repeatedly with consistent results.

The counting technique was the same as above. However, both iodine and barium samples were counted immediately after purification.

The chemical extraction was the same as used for I^{131} .

(c) Barium

The activity of the I^{131} was compared with that of Ba^{140} and that of the 54 min. iodine with that of Ba^{139} , both barium activities being determined using aliquots of the various irradiated samples. In a previous paper (3) it was found that the fission yield for Ba^{140} was less than that indicated by studying the growth of the La^{140} daughter; this was due to a soft electron emission which was not counted in our arrangement. It should be noted that the fission yield for Ba^{140} which must be used for comparison purposes is the value experimentally obtained without correction, rather than the value determined from the growth of the La^{140} daughter.

Results

Table I gives the self-weakening and external absorption data for I^{131} and 54 min. I. The activities found in Ba^{140} , I^{131} , Ba^{139} , and 54 min. I are shown in Tables II and III. The fission yields of the two iodines are given, having been obtained from the Ba data. Table IV gives the fission yields of masses 131, 132, 134, and 136 calculated from the data of Thode (6) with reference to I^{131} . In Table V are shown the properties of the I fission fragments.

The activities found in Ba^{140} , I^{131} , Ba^{139} , and 54 min. I are given below in Tables II and III as counts per gram uranium oxide irradiated.

Discussion

The difference in fission yields for masses 131 and 134 between fast and slow fission is so small, and the accuracy of our measurements is of such an order, that it is possible to neglect the fact that a relatively considerable portion of fast fissions must have occurred in the metal studied by Thode. A comparison of Tables III and IV would indicate that a mass number of 134 can be assigned to the 54 min. iodine. It should be pointed out that this will be true whatever the absolute value set for the Ba^{139} , Ba^{140} , and I^{131} fission yields.

TABLE II
FISSION YIELDS OF I^{131}

Isotope	Trial 1, counts/min.	Trial 2, counts/min.	Fission yields, $\times 10^{-2}$	Remarks
Ba^{140} I^{131}	145 73	142 76	4.3 (4) $2.23 \pm .11$	Thermal neutrons
Ba^{140} I^{131}	31 23	31 21	3.2 (4) $2.27 \pm .11$	Fast neutrons

¹ All data were corrected for self-weakening, absorption by the counter window and air gap, saturation of bombardment, decay, and for percentage recovery.

TABLE III
FISSION YIELDS OF 54 MIN. IODINE¹

Isotope	Graphite ²		Paraffin		Remarks
	Counts/min. (average of two results)	Fission yield, $\times 10^{-2}$	Counts/min. (average of two results)	Fission yield, $\times 10^{-2}$	
Ba^{139} $I^?$	2088 1987	6.1 (4) $5.80 \pm .10$	500 466	6.1 (4) $5.70 \pm .25$	Thermal neutrons
Ba^{139} $I^?$	79 98	5.1 (4) $6.32 \pm .12$	167 173	5.1 (4) $5.28 \pm .23$	Fast neutrons

¹ All data were corrected for self-weakening, absorption by the counter window and air gap, saturation of bombardment, decay, and for percentage recovery.

² Corrections were also made for variations in source intensity as monitored by In.

TABLE IV
FISSION YIELDS CALCULATED FROM XENON DATA OF THODE AND
GRAHAM (6) AND FISSION YIELD OF I^{131} (2.23%)

Mass number	Relative abundance (6)	Fission yields, (calc.) $\times 10^{-2}$
131	13.7	(2.23)
132	20.4	3.31
134	36.0	5.85
136	29.8	4.85

The following Table V gives a summary of the properties of the iodine fission fragments as they now appear to us, according to the above experiments.

TABLE V
PROPERTIES OF IODINE FISSION FRAGMENTS

Mass	Half-life	$\epsilon_{1/2}$ mgm./cm. ²	$\eta_{1/2}$ mgm./cm. ²	Fission yield, $\times 10^{-2}$		
				This report	Thode	Fermi <i>et al.</i>
129	Quite long ¹	—	—	—	—	—
131	8.0 days	22	56	2.23	2.23 ²	1.6
132	2.4 hr.	—	—	—	3.31	5.2
133	22 hr.	42 (2)	100 (2)	—	—	—
134	54 min.	98	151	5.75	5.85	12.0
135	6.6 hr.	—	—	—	—	—
136	1.8 min.	—	—	—	4.85	—

¹ This may be inferred because

(a). Its activity has not been detected, while Te^{129} is known to be β -active, and Xe^{129} is stable, and,

(b). Thode has not found in fission Xe the mass 129 with an abundance high enough to account for the complete decay of Te^{129} (half-life 72 min. and a 32-day isomer).

² Reference fission yield.

Acknowledgment

The authors wish to express their gratitude to J. Guéron (now with the French Atomic Energy Project), who took a keen interest in this work, for the many suggestions and interesting discussions which took place.

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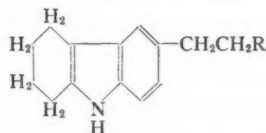
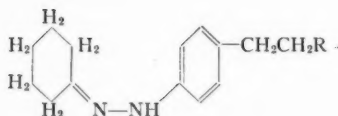
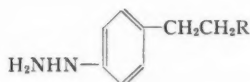
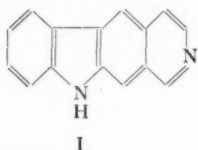
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THE SYNTHESIS OF SOME CARBAZOLE DERIVATIVES¹BY RICHARD H. F. MANSKE² AND MARSHALL KULKA³

Abstract

In attempts to synthesize 10-pyrido(3,4-*b*)carbazole, a number of new compounds were prepared. These are β -(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid, β -(5,6,7,8-tetrahydro-3-carbazolyl)ethylamine and their intermediates.

The compound, 10-pyrido(3,4-*b*)carbazole (I), does not appear to have been described. It was needed in connection with another problem and attempts were made to prepare it. Thus far, success has not attended these efforts but a number of new compounds of interest in themselves were synthesized and these are now described.



When 4-hydrazino- β -phenylpropionic acid (II) was condensed with cyclohexanone and the resulting phenylhydrazone (III) subjected to the Fischer indole ring closure a good yield of β -(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid (IV) was obtained. In an attempt to convert (IV) to β -(5,6,7,8-tetrahydro-3-carbazolyl)ethylamine (VIII), the urethane of IV was prepared via the hydrazide, azide, and isocyanate successively and the urethane was fused with phthalic anhydride. The resulting oily material was not the required β -(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (VII) since it did not produce any acid-soluble material when subjected to hydrolysis, according to the method of Ing and Manske (5). (VIII) was ultimately obtained from β -(4-hydrazinophenyl)ethylphthalimide (V) via its condensation with cyclo-

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hexanone, Fischer indole ring closure of the resulting (VI), and hydrolysis of the phthalimide (VII).

Attempts to effect ring closure of the N-formyl, N-carbethoxy, and N-acetyl derivatives of (VIII) by means of phosphorus oxychloride failed. The tetrahydrocarbazole derivatives (IV) and (VII) could not be dehydrogenated under the conditions used. When heated at 230° C. with platinum oxide (VII) was recovered unchanged while (IV) yielded neutral material.

Experimental

p-Nitrohydrocinnamic Acid (1)

To a stirred solution of hydrocinnamic acid (200 gm.) in glacial acetic acid (100 cc.) was added dropwise fuming nitric acid (400 gm.) over a period of one hour. The temperature of the reaction mixture was maintained at 20° to 25° C. by means of a cold water bath. The reaction mixture was allowed to stand at room temperature for three hours with occasional cooling at first, and then poured into one litre of cold water. The yellow solid was filtered, washed with water, and recrystallized from ethanol. The yield of light-yellow needles was 94.5 gm. or 37%; m.p. 164° to 165° C.*

p-Aminohydrocinnamic Acid (3)

A hot solution of *p*-nitrohydrocinnamic acid (20 gm.) in 4 *N* ammonium hydroxide (100 cc.) was added to a boiling solution of ferrous sulphate heptahydrate (200 gm.) in water (400 cc.). The reaction mixture was treated with concentrated ammonium hydroxide until strongly alkaline, boiled for three minutes, more ammonium hydroxide (10 cc.) added, and the boiling continued for another two minutes. The black precipitate was filtered off under suction, the hot filtrate concentrated to about 250 cc., treated with charcoal, and filtered again. The filtrate on acidification with acetic acid and on cooling deposited white needle-like crystals (15.2 gm. or 90%), m.p. 131° to 132° C.

p-Hydrazinohydrocinnamic Acid (II)

To a solution of *p*-aminohydrocinnamic acid (28.0 gm.) in concentrated hydrochloric acid (45 cc.) and water (100 cc.) cooled below 0° C. was added a cold solution of sodium nitrite (11.0 gm.) in water (35 cc.) over a period of 10 min., the temperature of the reaction mixture being kept below 0° C. The resulting diazonium salt solution was added as quickly as possible to a chilled solution of sodium sulphite (110 gm.) in water (200 cc.). The amber solution was allowed to warm up gradually to room temperature, heated at 75° to 80° C. for three hours, acidified strongly with concentrated hydrochloric acid, heated for a further five hours, and cooled. The precipitated hydrazine hydrochloride was filtered, dissolved in a minimum amount of hot water, made alkaline with concentrated ammonium hydroxide, and adjusted to pH 5 with acetic acid. The precipitated hydrazine (23 gm. or 75%) was filtered off from the cooled solution, washed with a little cold water and dried, m.p. 158°

* All melting points are corrected.

to 160° C. (decomposition), recrystallized from ethanol, m.p. 158° to 160° C. (decomposition). Calc. for $C_9H_{12}O_2N_2$: C, 60.00; H, 6.72; N, 15.56%. Found: C, 60.28, 60.37; H, 6.72, 6.57; N, 15.72, 15.53%.

Hydrazone of p-Hydrazinohydrocinnamic Acid and Cyclohexanone (III)

To *p*-hydrazinohydrocinnamic acid (23 gm.) dissolved in ethanol (350 cc.) was added cyclohexanone (11.0 gm.) and the resulting solution heated under reflux for five hours. The solution on concentration to about 200 cc. and cooling yielded yellow-orange needles (25 gm. or 75%) melting at 156° to 158° C. with decomposition. Calc. for $C_{15}H_{20}O_2N_2$: C, 69.20; H, 7.75; N, 10.76%. Found: C, 69.29, 69.21; H, 7.57, 7.86; N, 10.83, 10.93%.

β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionic Acid (IV)

The hydrazone of *p*-hydrazinohydrocinnamic acid and cyclohexanone (III) (8.8 gm.) was ground up to a fine powder and added to 17% by weight sulphuric acid (90 cc.) previously warmed up to 50° C. Most of the fine powder dissolved, and after a few minutes' stirring, a precipitate began to appear. The reaction mixture was heated on a water-bath at 65° to 70° C. for one hour, cooled, and the precipitate filtered and washed with water. Crystallization from methanol containing a little water yielded white needles (5.7 gm. or 70%), m.p. 118° to 120° C. Calc. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.05; N, 5.76%. Found: C, 74.02, 73.82; H, 7.19, 6.94; N, 5.76, 5.94%.

Methyl β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionate

To β-(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid (3.5 gm.) dissolved in methanol (70 cc.) was added (1.8 gm.) concentrated sulphuric acid and the solution heated under reflux for six hours. To the cooled solution was added sodium bicarbonate (4 gm.) dissolved in water (30 cc.) and the methanol removed under reduced pressure. The precipitated ester (3.4 gm. or 92%) was filtered, washed with water, and dried, m.p. 76° to 78° C.; recrystallized from methanol-water m.p. 76° to 78° C. Calc. for $C_{16}H_{19}O_2N$: C, 74.71; H, 7.39; N, 5.32%. Found: C, 74.40, 74.50; H, 7.17, 7.20; N, 5.44, 5.46%.

β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionic Hydrazide

A solution of methyl β-(5,6,7,8-tetrahydro-3-carbazolyl)propionate (1.0 gm.), methanol (3 cc.) and hydrazine hydrate (1.5 cc.) was heated on the steam-bath, the methanol being allowed to distil off. After five hours' heating (0.5 cc.) more of hydrazine hydrate was added and the heating continued for another hour. The precipitated white solid (1.1 gm.) was filtered, washed with water, and dried. Recrystallization from ethyl acetate yielded yellowish microscopic crystals, m.p. 159° to 160° C. Calc. for $C_{15}H_{19}N_3O$: C, 70.04; H, 7.39; N, 16.34%. Found: C, 69.51, 69.35; H, 7.35, 7.25; N, 16.45, 16.12%.

β-Phenylethylphthalimide

This was prepared by fusing β-phenylethylamine (2) with phthalic anhydride. It had the same melting point as that reported in the literature (5).

β -p-Nitrophenylethylphthalimide

To stirred fuming nitric acid (*d.*, 1.5, 210 cc.) was added β -phenylethylphthalimide (85 gm.) over a period of 30 min., the temperature of the reaction mixture being kept at 20° to 25° C. by cooling. After allowing the reaction mixture to stand at room temperature for five hours, it was poured into cold water. The yellow precipitate was filtered, washed well with water, and dried. Two successive crystallizations from benzene yielded stout light-yellow needles (49 gm. or 50%) melting at 203° to 204° C. Calc. for $C_{10}H_{12}O_4N_2$: C, 64.86; H, 4.05; N, 9.46%. Found: C, 65.05, 64.92; H, 4.18, 4.12; N, 9.65, 9.53%. This compound when mixed with that obtained by fusion of *p*-nitrophenylethylamine (4) with phthalic anhydride gave no melting point depression.

 β -p-Aminophenylethylphthalimide

A suspension of β -p-nitrophenylethylphthalimide (25 gm.) in ethanol (150 cc.) and 0.3 gm. of Adams platinum catalyst, was heated at 35° C. and shaken under an initial pressure of 40 lb. of hydrogen for 24 hr. Then the temperature was raised to 60° C. and the hydrogenation continued for another six hours, at the end of which time reaction was complete. To the reaction mixture about 250 cc. ethanol was added, and the whole heated until all the organic material dissolved, and then filtered. On cooling, the filtrate deposited yellow prisms (18.6 gm. or 83%) in two successive crops, m.p. 155° to 156° C., recrystallized from ethanol, m.p. 156° to 157° C. Calc. for $C_{16}H_{14}O_2N_2$: C, 72.18; H, 5.26; N, 10.53%. Found: C, 72.33, 72.37; H, 5.24, 5.06; N, 10.67, 10.73%.

 β -p-Hydrazinophenylethylphthalimide (V)

β -p-Aminophenylethylphthalimide (5.0 gm.) was dissolved in hot water (150 cc.) containing concentrated hydrochloric acid (3 cc.), cooled, and to this was added concentrated hydrochloric acid (150 cc.). The reaction mixture was diazotized with a solution of sodium nitrite (1.30 gm.) in water (25 cc.), the temperature being kept below 0° C. After standing at 2° C. for eight hours, the reaction mixture was filtered to remove a small amount of undissolved material and the filtrate added as quickly as possible to a chilled solution of pure stannous chloride dihydrate (20 gm.) in concentrated hydrochloric acid (40 cc.). A white precipitate appeared immediately. The reaction mixture was allowed to stand at room temperature overnight and then filtered. The white solid was extracted with hot water (about 500 cc.) until no more dissolved, the extract treated with charcoal, filtered, and the hot filtrate basified with concentrated ammonium hydroxide and cooled. The yellow precipitate was filtered and recrystallized from ethanol, m.p. 165° to 166° C., yield 2.7 gm. or 50%. Calc. for $C_{16}H_{16}O_2N_2$: C, 68.33; H, 5.34; N, 14.95%. Found: C, 68.93, 68.75; H, 5.53, 5.54; N, 14.74, 14.98%.

Hydrazone of β -p-Hydrazinophenylethylphthalimide and Cyclohexanone (VI)

β -p-Hydrazinophenylethylphthalimide (4.0 gm.) was dissolved in hot ethanol (150 cc.), cyclohexanone (1.4 cc.) added, and the solution heated

under reflux for one-half hour. The yellow precipitate was filtered off from the cooled solution, washed, and dried; yield 4.7 gm. or 90%, m.p. 181° to 183° C. with decomposition. Recrystallization from ethanol gave golden-yellow needles, m.p. 181° to 183° C. with decomposition. Calc. for $C_{22}H_{23}O_2N_3$: C, 73.13; H, 6.37; N, 11.63%. Found: C, 72.94, 72.97; H, 6.51, 6.37; N, 11.78, 11.51%.

β -(5,6,7,8-Tetrahydro-3-carbazolyl) ethylphthalimide (VII)

The hydrazone of β -*p*-hydrazinophenylethylphthalimide (6.2 gm.) (VI) was added to 17% by weight sulphuric acid (125 cc.) and heated on the steam-bath for one and a quarter hours with occasional stirring. The reaction mixture was diluted with water, filtered, washed, and dried. Recrystallization from ethanol yielded yellow needles (5.02 gm. or 85%) melting at 219° to 221° C.; recrystallized from ethyl acetate, m.p. 221° to 222° C. Calc. for $C_{22}H_{20}O_2N_2$: C, 76.74; H, 5.86; N, 8.14%. Found: C, 76.51, 76.53; H, 5.78, 5.89; N, 8.32, 8.32%.

β -(5,6,7,8-Tetrahydro-3-Carbazolyl) ethylamine (VIII)

To a solution of β -(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (3.5 gm.) in ethanol (100 cc.) was added hydrazine hydrate (7 cc.) and the solution heated under reflux for one-half hour. To the cooled solution concentrated hydrochloric acid (35 cc.) was added and the resulting solution heated to boiling and then taken almost to dryness under reduced pressure. To the residue water was added, and the white insoluble phthalylhydrazide was filtered and washed with dilute hydrochloric acid. The combined filtrate and washings were basified with sodium hydroxide and extracted with ether. Removal of the ether yielded a yellow oil (1.75 gm. or 80%) which distilled at about 220° C. (2 mm.). It would not crystallize on cooling and scratching. Calc. for $C_{14}H_{15}N_2$: C, 78.45; H, 8.42%. Found: C, 78.12, 78.01; H, 8.35, 8.30%. This amine when heated with phthalic anhydride at 230° C. for a few minutes yielded a compound melting at 219° to 222° C., which did not depress the melting point of β -(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (VII).

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THE PREPARATION, PURIFICATION, PHYSICAL PROPERTIES AND HYDROLYSIS OF CYANOGEN CHLORIDE¹

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Abstract

Cyanogen chloride, prepared by the method of Jennings and Scott, has been fractionally recrystallized to a constant freezing point of -6.90°C . Vapour pressure values for material purified in this way are in good agreement with the data of Klemenc and Wagner. The activation energy for the hydrolysis of cyanogen chloride at pH 4 to 6 between 0° and 50°C . is approximately 21 kcal. per mole.

This paper deals with the preparation, purification, and some physical properties of cyanogen chloride, together with a note on its hydrolysis in aqueous solution.

Experimental

Preparation and Purification of Cyanogen Chloride

Cyanogen chloride was prepared by the method of Jennings and Scott (2) from 200 gm. of sodium cyanide conditioned to approximately 2% moisture, and suspended in 300 ml. carbon tetrachloride. Chlorine was passed into this mixture for 8 to 12 hr., at such a rate that the temperature did not rise above 0°C . Efficient cooling and stirring of the reaction mixture were necessary, and care had to be taken that all the sodium cyanide had reacted before the passage of chlorine was stopped and distillation begun, otherwise loss of cyanogen chloride took place through reaction with sodium cyanide to form a black solid. The reaction vessel was cooled in an ice-salt bath, and the contents was stirred mechanically.

When the reaction was judged to be complete, a fractionating column and calcium chloride drying tube were fitted to the reaction flask, which was warmed to 15° to 20°C . by means of a water-bath that could be heated near the end of the distillation. In early preparations, the fractionating column was a water-jacketed condenser, the inner tube of which was packed with a series of glass disks, and about which water at 13° to 14°C . was circulated, but later, a simple tube about 18 in. long filled with copper gauze was employed with satisfactory results. The gaseous cyanogen chloride was condensed, after passing through the fractionating column and calcium chloride tube, in a trap or large ampoule immersed in an ice-bath. Distillation was stopped when the temperature in the reaction flask rose to 40°C . If the distillate contained free chlorine, as indicated by a greenish colour, mercury was added to the liquid, and it was shaken occasionally. The cyanogen chloride was distilled off from the residue.

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Several methods of purifying cyanogen chloride reported in the literature were tried without success. Fractional distillation at reduced pressure at -78°C . did not remove the last traces of chlorine, and distillation through a suspension of zinc oxide and calcium carbonate caused a lowering of the freezing point of a fairly pure sample of cyanogen chloride. Chlorine was not removed satisfactorily by arsenic, antimony, or zinc metal. The material was finally purified by fractional crystallization of the distillate from the Jennings and Scott preparation.

The water-white distillate was frozen in the trap or ampoule used as a receiver, until it was 80 to 90% solid. The mother liquor was poured off, the solid remelted, and crystallization was repeated until no further rise in the freezing point occurred. In a typical purification, the freezing point rose from -7.73°C . after the first crystallization to a constant value of -6.90°C . after the third recrystallization. Usually three recrystallizations of redistilled cyanogen chloride were sufficient to give a product better than 99.5% pure.

Determination of Purity of Cyanogen Chloride

The purity of the cyanogen chloride was determined by the methods of Mauguin and Simon (4). The first of these involves hydrolysis of cyanogen chloride in an excess of standard sodium hydroxide and back-titration with standard sulphuric acid to a phenolphthalein end-point, care being taken not to make the solution acid:



Alternatively, in the presence of a measured excess of sulphuric acid, hydrolysis of the cyanic acid occurs, and the sulphuric acid can be back-titrated with standard base in the presence of methyl red when hydrolysis is complete:



A third method was used, in which chloride was titrated with 0.03 *N* silver nitrate in the presence of dichlorofluorescein after hydrolysis of the cyanogen chloride.

Two methods were employed to get an accurately known weight of cyanogen chloride absorbed in sodium hydroxide. In Method *A*, a convenient quantity of cyanogen chloride at 0°C . was poured into 50 ml. of 0.5 *N* carbonate-free sodium hydroxide cooled to 0°C . The flask and contents were weighed at room temperature and atmospheric pressure before and after the addition of the cyanogen chloride. In Method *B*, the cyanogen chloride was sealed in a small vial with a long tip which could be broken off by pressure on a stopper after the vial had been placed in a flask containing sodium hydroxide. The weight of the vial was found by collecting and weighing the fragments.

Freezing Point Determinations

The method employed for freezing point determinations was an extension of that used by Morrison and Grummitt (5). The sample under investigation was contained in a small clear Dewar flask to which was sealed a stopcock at

the top by means of which the air pressure between the walls could be adjusted to give a convenient rate of cooling when the Dewar flask was immersed in an ice-salt mixture at about -12°C . This vessel was fitted with a Beckmann thermometer and mechanically driven ring stirrer. The Beckmann thermometer was compared with two standard thermometers of different ranges. The zero points of these were checked with great care.

The vessel containing the sample of cyanogen chloride was placed in the ice-salt mixture, and time-temperature readings were taken until the freezing point had been passed. An ice-water bath was then substituted for the ice-salt mixture and readings were taken as before.

The cooling curve was of the conventional type for a pure compound. The freezing point could be determined accurately, but the melting point was not well defined.

In Table I, analytical and freezing point data are given for a series of samples of cyanogen chloride.

The molal freezing point lowering for cyanogen chloride was determined by measuring the freezing point depression produced when 0.7018 gm. of carbon

TABLE I
FREEZING POINT DATA AND PURITY OF CYANOGEN CHLORIDE BY CHEMICAL ANALYSIS

Freezing point, $^{\circ}\text{C}$.	Sample weight by method	Percentage purity		
		(1) By NaOH used	(2) By NH_3 produced	(3) By Cl present
-6.90	(1) 0.5645 <i>A</i>	100.9	—	—
	(2) 0.6375 <i>A</i>	100.5	—	—
	(3) 0.5517 <i>A</i>	101.0	—	—
-6.92	(1) 0.4742 <i>A</i>	101.8	—	—
	(2) 0.4529 <i>A</i>	100.7	—	—
	(3) 0.5062 <i>A</i>	100.2	—	—
-7.25	(1) 0.4342 <i>A</i>	98.8	—	—
	(2) 0.4722 <i>A</i>	99.2	—	—
	(3) 0.4527 <i>A</i>	99.3	—	—
-7.32	(1) 0.6647 <i>B</i>	100.3	—	—
	(2) 0.4770 <i>B</i>	96.5	—	—
	(3) 0.6970 <i>B</i>	96.2	—	—
-7.00	(1) 0.6218 <i>A</i>	99.67	—	99.8
	(2) 0.5476 <i>A</i>	99.90	—	100.8
-7.00	(1) 0.6006 <i>B</i>	99.85	99.9	99.4
	(2) 0.5758 <i>B</i>	99.10	98.9	99.4
-6.92	(3) 0.4878 <i>B</i>	99.55	99.5	99.2
	(1) 0.8762 <i>A</i>	99.88	—	100.5
	(2) 0.7169 <i>A</i>	100.32	—	100.2
-10.50	(1) 0.6039 <i>A</i>	89.3	—	—
	(2) 0.6445 <i>A</i>	88.6	—	—
	(3) 0.6134 <i>A</i>	88.1	—	—

tetrachloride was added to 24.186 gm. of cyanogen chloride. A lowering of 0.60° C. for a molality of 0.1886 was found, and the molal freezing point lowering is therefore 3.18° C. (calculated for CNCl , 3.19° C.). If the latent heat of fusion is assumed to be constant between -6.92° and -7.52°C. , its value is 2720 cal. per mole. The entropy of fusion is 10 entropy units.

Vapour Pressure Measurements

The vapour pressure of cyanogen chloride was measured at various temperatures by a static method. A trap containing cyanogen chloride, and fitted with an Anschutz thermometer was connected to a mercury manometer. The trap was surrounded by a bath at the desired temperature contained in a Dewar flask. Readings were taken over such long periods of time that equilibrium was established between the cyanogen chloride and the bath, and the temperature of the cyanogen chloride was taken as that of the bath with only slight error. Observations were made over a period of nearly a week. The data, together with those of Klemenc and Wagner (3), are given in Table II.

The latent heat of vaporization calculated from the slope of the $\log p$ vs. $\frac{1}{T}$ line, using the Clausius-Clapeyron relation, is 6400 cal. per mole.

TABLE II
VAPOUR PRESSURE DATA FOR CYANOGEN CHLORIDE

Temperature, ° C.	Vapour pressure, mm. of Hg	
	Present values	Data of Klemenc and Wagner
-12	—	233
-10	—	265
-8	—	302
-6	342.1	341
-5.6	348.3	—
-4.8	359.1	—
-4.0	—	373
-2.8	396.3	—
-2.0	—	408
0.00	446.8	445
0.00	446.5	—
1.85	483.6	—
2.00	—	484
3.40	515.4	—
4.00	—	527
5.00	558.0	—
6.00	—	573
6.20	581.2	—
7.40	616.5	—
8.00	—	621
9.10	658.3	—
10.00	—	674
10.60	697.3	—
12.00	—	730
12.80	754.8	—
13.00	763.0	—
14.00	—	790
17.82	916.5	—

The Hydrolysis of Cyanogen Chloride

Using material prepared as described previously, a brief study was made of the hydrolysis of cyanogen chloride in aqueous solutions buffered with carbon dioxide (pH 4 to 6). The steps in this reaction are (6, 7):



In solutions of pH less than 7, hydrolysis of cyanic acid is rapid at ordinary temperatures, and the first reaction is rate governing. A freshly prepared solution of pure cyanogen chloride was found to give no significant amount of precipitate with silver nitrate, hence the progress of reaction was followed by titration of chloride ion.

Portions of a freshly prepared solution of cyanogen chloride in distilled water saturated with carbon dioxide (pH between 4 and 6) were sealed into bulbs (all glass) and placed in thermostats controlled to $\pm 0.05^\circ \text{C}$. The initial concentration of cyanogen chloride was determined by complete hydrolysis with excess 0.5 *N* sodium hydroxide solution and back-titration of the excess alkali to phenolphthalein end-point. The blank on the water saturated with carbon dioxide was also determined by adding excess standard alkali and back titrating. The extent of chloride ion formation after different periods of hydrolysis was determined by titration with 0.3 *N* silver nitrate, using dichlorofluorescein indicator.

Experiments were made without duplication for the following conditions:

Temperature, ° C.	Initial concentration, molarity	Extent of reaction studied, %
0.0	0.040	5
11.1	0.078	5
30.0	0.081	18
30.0	0.184	11
40.0	0.078	18
40.0	0.087	20
40.0	0.141	21
50.0	0.070	33
50.0	0.124	33

Data for 40°C ., given in Table III, are typical of those obtained at other temperatures except 11.1°C ., where for no obvious reason, somewhat greater variation about a straight line was noted when $\log \frac{[\text{CNCl}]_{\text{initial}}}{[\text{CNCl}]_t}$ was plotted against time to yield the corresponding k values.

TABLE III
TYPICAL DATA FOR HYDROLYSIS OF CYANOGEN CHLORIDE AT 40° C.
Initial concentration, moles per litre

0.078		0.087		0.141	
Time, hr.	[CNCI] _t , moles/litre	Time, hr.	[CNCI] _t , moles/litre	Time, hr.	[CNCI] _t , moles/litre
4.6	0.075	3.4	0.084	3.4	0.136
6.8	0.073	9.6	0.079	9.6	0.128
17.5	0.065	13.1	0.076	13.1	0.123
—	—	18.0	0.072	18.0	0.117
—	—	23.5	0.069	23.5	0.110

The data indicate clearly that, over the limited range studied, the reaction was first order. The variation in first order rate constant with temperature may be summarized as follows:

Temperature, ° K.	<i>k</i> , hr. ⁻¹
273.0	8.6×10^{-5}
284.1	3.1×10^{-4}
303.0	3.6×10^{-3}
313.0	1.2×10^{-2}
323.0	3.1×10^{-2}

A plot of $\log k$ vs. $\frac{1}{T}$ yielded an activation energy for the hydrolysis of approximately 21 kcal. per mole.

The addition of ammonium chloride to the extent of 0.01 *M* to two solutions of initial cyanogen chloride concentrations 0.052 *M* and 0.108 *M* gave no significant change in rate at 40° C. The addition of potassium nitrate in similar amount to a solution 0.056 *M* in cyanogen chloride resulted in approximately 25% increase in rate. Duplicate experiments were not made, but the effect of potassium nitrate is probably genuine.

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STUDIES ON THE FORMATION OF HEXAMINE¹

MARY L. BOYD² AND C. A. WINKLER³

Abstract

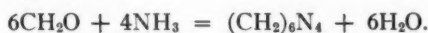
Rate curves have been determined for the reaction of ammonia and formaldehyde in aqueous solution at 0° C. and 35° C., over a range of initial mole ratios (formaldehyde: ammonia) of 0.25 to 2.0. For each set of conditions, three curves have been obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride respectively.

At 0° C. the three rate curves tend to approximate one another in a large excess of ammonia but are widely separated in excess formaldehyde. The reverse is true at 35° C. The reaction is characterized by a high initial rate of formation of hexamine, this rapid rate being maintained to a lower yield of hexamine the more dilute the solution. The existence of a stable by-product in excess formaldehyde is indicated by the variation in final yields of hexamine, when these are calculated on the basis of formaldehyde consumed, ammonia consumed, or material precipitated with mercuric chloride.

A mechanism for the reaction has been suggested.

Introduction

The only kinetic study of the reaction of formaldehyde with ammonia in aqueous solution to form hexamethylenetetramine (hexamine) was made by Baur and Rüetschi (1) in 1941. Their investigation showed that practically complete reaction took place and that the 'over-all' reaction could be represented by the equation:



The course of the reaction was followed by an acid titration of the ammonia. On the basis of rate constants calculated from the consumption of ammonia, Baur and Rüetschi (1) concluded that the reaction was third order with ammonia and formaldehyde in the molar ratio of 1:2.

A more complete study of the reaction between formaldehyde and ammonia in aqueous solution has been made, in which the rate of appearance of hexamine was followed simultaneously with the rate of disappearance of both formaldehyde and ammonia. These data should indicate whether there is any by-product formation and so present a more complete insight into the reaction of formaldehyde with ammonia in aqueous solution.

Experimental

Rate curves were determined at 0° C. and at 35° C. over a range of initial mole ratios (formaldehyde: ammonia) of 0.25 to 2.0. For each set of conditions, three curves were determined on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride.

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The reaction was studied in 125 ml. stoppered Erlenmeyer flasks in an ice-bath (0°C.) and in a constant temperature water-bath maintained at 34.9°C. Ammonia solution (25 ml.) of the required strength was pipetted into the Erlenmeyer flasks, which were placed in the thermostat and allowed to come to the temperature of the bath. Formaldehyde solution (25 ml.) of the required strength, at the same temperature as the ammonia solution, was then added to each ammonia sample. Zero time was taken as the mid-point of the time required to drain the pipette. The reaction mixtures were shaken (to expedite removal of heat) for the desired times, after which the reaction was stopped with nitric acid ($0.1\text{ }N$). The end-point of the reaction was taken as the mid-point in the time required to make this acid titration. The sample was immediately placed in a 100 ml. volumetric flask and diluted to 100 ml. A 25 ml. aliquot was analysed for formaldehyde and a 50 ml. aliquot, for hexamine. The length of time between the end of the reaction (the acid titration) and the hexamine and formaldehyde analyses never exceeded three minutes. Preliminary experiments showed that there was no hexamine formed by the resulting ammonium nitrate and formaldehyde in the time required for these analyses.

Preparation of Reactants

Aqueous ammonia solutions were made by diluting reagent grade concentrated ammonia to the required strength and analysing the resulting solutions by acid titration with nitric acid ($0.1\text{ }N$).

Formaldehyde solutions were made by subliming paraformaldehyde into water. The resulting solutions were analysed by the potassium cyanide method.

Analytical Methods

The residual ammonia in the reaction mixture was determined by the acid titration, which also served to stop the reaction. Phenol red (pH range 6.8 to 8.4) was used as an indicator to avoid titration of the hexamine present. Preliminary experiments showed that hexamine was not titrated under these conditions.

The residual formaldehyde in the reaction mixture was determined by the potassium cyanide method. This is one of the standard methods of analysing for formaldehyde. The following technique was used. The 25 ml. aliquot of the diluted reaction mixture was introduced into an Erlenmeyer flask and to it a drop of phenolphthalein solution was added. It was necessary to add one or two drops of sodium hydroxide ($0.1\text{ }N$) to make the solution alkaline to phenolphthalein. Then a known volume of potassium cyanide ($0.1\text{ }N$) was added; usually 5 to 10 ml. in excess of that required to react with the formaldehyde present. The mixture was shaken and a known volume of silver nitrate ($0.1\text{ }N$) containing 20% nitric acid was added. The silver cyanide was filtered off and the filtrate titrated with potassium thiocyanate ($0.1\text{ }N$) using ferric alum as indicator. Preliminary experiments showed that the presence of hexamine does not affect the formaldehyde analysis.

The method of analysis for hexamine is based on the fact that hexamine and mercuric chloride form an insoluble complex (2, 3, 4). The method used is purely an empirical one and consists of precipitating hexamine under constant conditions. A calibration curve was established between known weights of hexamine in distilled water and the corresponding weights of the complex formed. Formaldehyde in amounts corresponding to its presence in the reaction mixture were without effect on the calibration curve, but the mercury-hexamine precipitate in the presence of excess ammonium ion was contaminated to the extent of about 2% by weight. A 50 ml. aliquot of the reaction solution, after titration with acid, was placed in an Erlenmeyer flask and 50 ml. water added, followed by 50 ml. mercuric chloride solution saturated at 40° C. After one-half hour, the precipitate was collected on a tared, sintered glass crucible, dried for one hour at 100° C., cooled, and weighed. The weight of hexamine was read from the calibration curves established under these reaction conditions.

Preliminary experiments showed that reaction-time data were reproducible to within approximately $\pm 1.5\%$ by the analytical methods used for ammonia and hexamine, and to within $\pm 3\%$ by formaldehyde analysis.

Results

Experiments were made at 0° C. to determine the effect of (i) changes in initial concentrations when the initial mole ratio is constant, and (ii) changes in the initial mole ratio with the initial concentration of formaldehyde or ammonia constant. The rate curves are plotted in Figs. 1, 2, and 3. The yield of hexamine is expressed as a percentage of the theoretical amount of hexamine for each particular set of initial concentrations. This theoretical yield is calculated on the basis of the initial concentration of that reactant which is not in excess. The three rate curves obtained for each experimental condition may be referred to, for convenience, as the ammonia curve, the formaldehyde curve, and the hexamine curve, when the yield is calculated on the ammonia consumed, the formaldehyde consumed, and the hexamine precipitated with mercuric chloride respectively.

The data reveal that under certain conditions there is a wide separation in the rate curves. Since all three curves are expressed in terms of hexamine, it is apparent that their separation demands interpretation of the analytical data.

The ammonia curve, which generally lies above the other two curves (but not in *A* and *B*, Fig. 2), would seem to correspond to a total of hexamine plus intermediates, the acid titration failing to titrate back the ammonia associated with the intermediates. Thus the consumption of ammonia, when expressed as hexamine, might logically correspond to curves of the type observed.

Where formaldehyde is in excess (Fig. 1) and also in two cases where ammonia is in excess (Curves *A* and *C*, Fig. 3), it is noted that the formaldehyde curve falls below the other two. This can be explained if, in the

analysis for the residual formaldehyde in the reaction mixture, formaldehyde were analysed out of intermediates. If this analysis of formaldehyde out of intermediates but not out of hexamine itself be quantitative, the curve based on the consumption of formaldehyde should represent, to a good approximation, the actual rate of formation of hexamine. It follows from this argument,

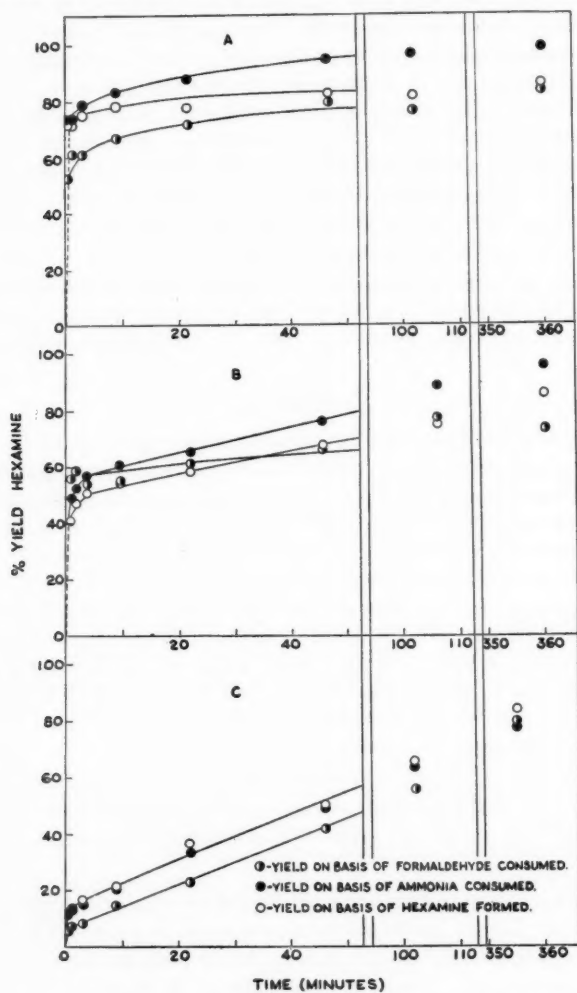


FIG. 1. Rate curves for reaction at 0°C . Curves A—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 1.88; initial concentrations—0.195 mole per litre ammonia, 0.367 mole per litre formaldehyde. Curves B—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 1.85; initial concentrations—0.0964 mole per litre ammonia, 0.179 mole per litre formaldehyde. Curves C—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 1.96; initial concentrations—0.0502 mole per litre ammonia, 0.0984 mole per litre formaldehyde.

that when the hexamine curve lies above the formaldehyde curve, the mercuric chloride must precipitate something other than hexamine. Since the three curves generally do not converge at the end-point, it may be assumed that a stable by-product is formed.

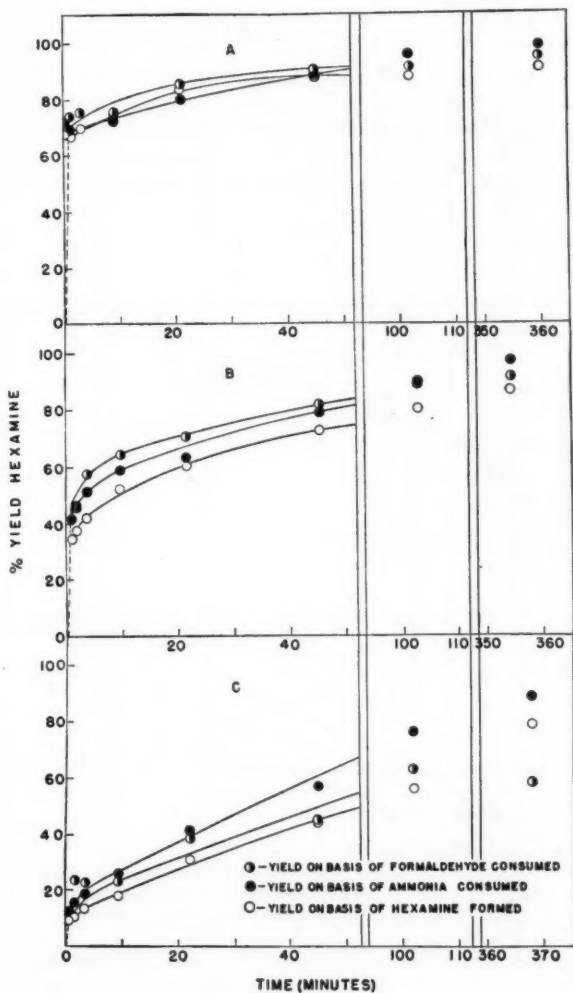


FIG. 2. Rate curves for reaction at 0° C. Curves A—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.25; initial concentrations—0.754 mole per litre ammonia, 0.190 mole per litre formaldehyde. Curves B—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.24; initial concentrations—0.398 mole per litre ammonia, 0.0968 mole per litre formaldehyde. Curves C—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.24; initial concentrations—0.194 mole per litre ammonia, 0.0475 mole per litre formaldehyde.

The relative positions of the formaldehyde curves indicate that, in the early stages of the reaction, the amount of formaldehyde consumed increases as the initial mole ratio (formaldehyde : ammonia) decreases. (Curves B, Fig. 1

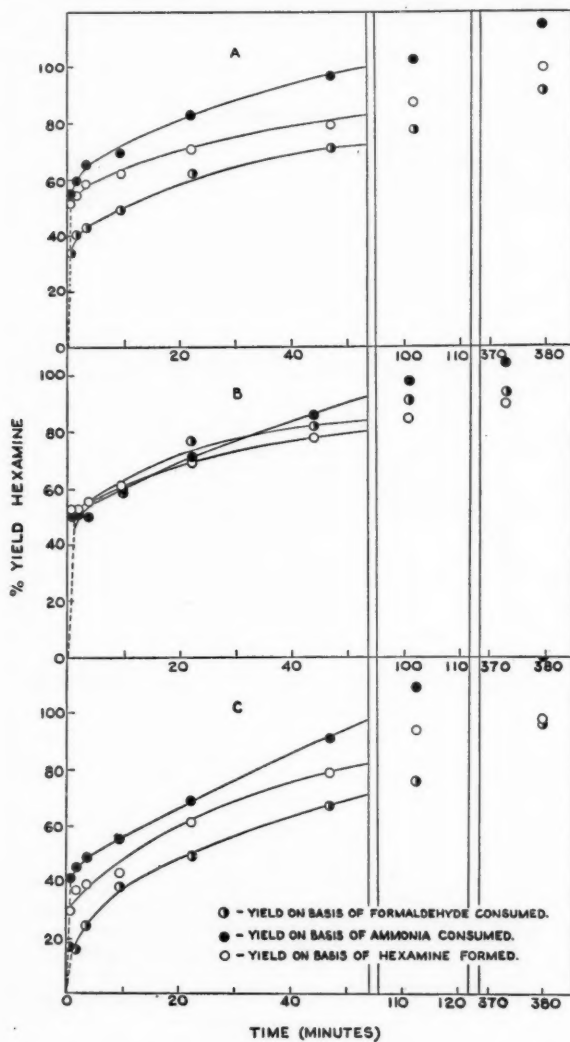


FIG. 3. Rate curves for reaction at 0° C. Curves A—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.94; initial concentrations—0.195 mole per litre ammonia, 0.183 mole per litre formaldehyde. Curves B—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.64; initial concentrations—0.280 mole per litre ammonia, 0.179 mole per litre formaldehyde. Curves C—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.46; initial concentrations—0.195 mole per litre ammonia, 0.0895 mole per litre formaldehyde.

and Curves C, Fig. 3 are exceptions). Following the argument outlined above, this means that as the formaldehyde curve moves upward, less and less formaldehyde is being analysed out of the intermediates, and this, in turn, indicates that the reaction may take place along at least two different paths. Along the path which is preferred when formaldehyde is in excess, formaldehyde is analysed out of the intermediates, whereas along the path preferred when ammonia is in excess, the amount of formaldehyde analysed back from the intermediates is less.

In the series of experiments where the initial mole ratio was kept constant at 2.0 and in a second series where the initial mole ratio was constant at 0.25, it is noted that the high initial rate of formation of hexamine is maintained to a lower yield of hexamine the more dilute the solution. (Figs. 1 and 2).

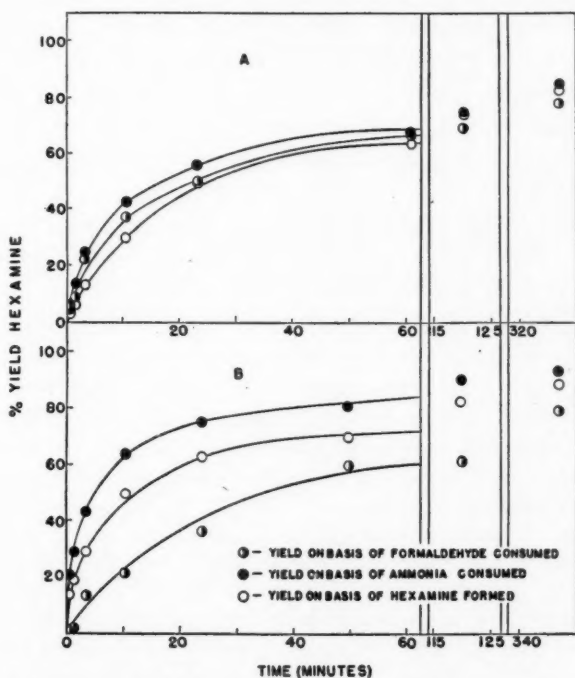


FIG. 4. Rate curves for reaction at 34.9° C. Curves A—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 2.03; initial concentrations—0.0507 mole per litre ammonia, 0.103 mole per litre formaldehyde. Curves B—initial mole ratio ($\text{HCHO} : \text{NH}_3$), 0.25; initial concentrations—0.208 mole per litre ammonia, 0.0520 mole per litre formaldehyde.

To investigate the effect of raising the temperature of the reaction, experiments were repeated at 34.9° C. The rate curves for these experiments are plotted in Fig. 4. The shape of the rate curves is quite different from that at 0° C. The rate in the early stages of the reaction is slower than at 0° C.

This would suggest that one route whereby hexamine was formed at 0° C. has been largely eliminated at 35° C. The effect of changing the initial mole ratio (formaldehyde : ammonia) at 35° C. is opposite to the effect produced by varying it at 0° C. For an initial mole ratio of 2.0, considerable formaldehyde is analysed out of the intermediates at 0° C. whereas a small amount is analysed out at 35° C., at comparable initial concentrations of formaldehyde and ammonia. Similarly, for an initial mole ratio of 0.25, a relatively small amount of formaldehyde is analysed back at 0° C. while at 35° C. a large amount is analysed out of the intermediates. The fact that two different types of curves were obtained at 35° C. would indicate that if two different paths exist, they have different activation energies.

A large number of samples of hexamine - mercuric chloride complex precipitated in the preceding experiments were analysed for formaldehyde and ammonia. The results showed that the complex is not contaminated with formaldehyde but is contaminated with ammonia to the extent of 2%.

Order of the Reaction

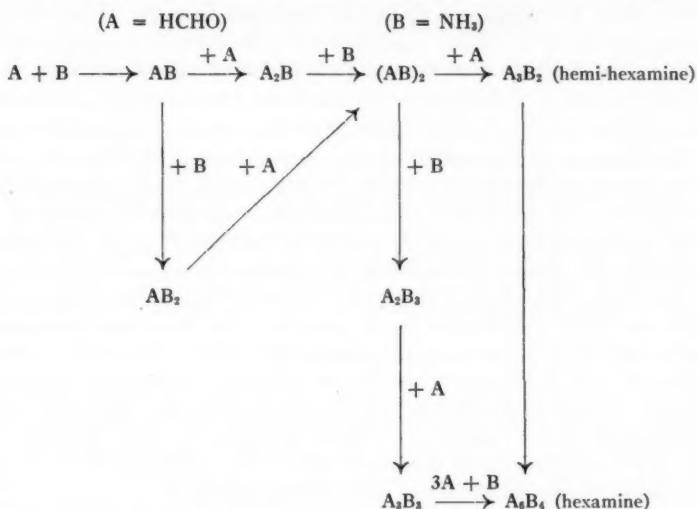
Baur and Rüetschi (1) considered the reaction between formaldehyde and ammonia in aqueous solution to be third order, the rate being proportional to $[\text{NH}_3] \times [\text{HCHO}]^2$.

The analytical data of the present study indicate that the reaction is complex. A determination of the order of the competing reactions would require many more kinetic data than are at present available.

Mechanism of the Reaction

The results of the present investigation indicate that any mechanism proposed for the reaction must account for several characteristics of the reaction. These are as follows:— (1) There is a high initial rate of formation of hexamine, this rapid rate being maintained to a lower yield of hexamine the more dilute the solution. This high initial rate is followed by a rapid transition to a much slower rate. (2) At 0° C., the rates of reaction inferred from the rates of disappearance of the two reactants and from the rate of formation of hexamine show discrepancies which indicate that at least two paths may lead to formation of hexamine, one path being preferred when ammonia is in excess, the other preferred when formaldehyde is in excess, and that more formaldehyde may be analysed back from intermediate bodies under these latter conditions. (3) Final yields of hexamine differ, depending upon whether they are calculated on the basis of ammonia consumed, formaldehyde consumed, or material precipitated with mercuric chloride. The implication is that a stable by-product may be formed under suitable conditions. (4) When the temperature was increased to 35° C. the consumption of formaldehyde, in the presence of excess formaldehyde, was greater relative to the consumption of ammonia than at 0° C., while in excess ammonia the reverse was true. Moreover, the effect of increased temperature was to reduce the rate of hexamine formation in the early stages of the reaction.

A two path type of mechanism may be illustrated by the following:—



This scheme is meant primarily to indicate possible alternative paths, and does not include all the reactions theoretically possible, nor is it particularly concerned with the steps leading to hexamine formation from the cyclic triamine and from hemi-hexamine. Disregarding the identity of the intermediate compounds postulated above, and assuming that the alternate paths lead from the dimer $(AB)_2$, the path to hemi-hexamine should be favoured in excess formaldehyde while that leading to A_3B_3 should be favoured in excess ammonia.

Additional postulates to account for the observed behaviour are: (1) rapid equilibrium between monomer and dimer; (2) formaldehyde but not ammonia, analysed from the dimer and monomer; and (3) an activation energy for the formation of the monomer that is less than that for reaction of the dimer with formaldehyde but greater than that for reaction of the dimer with ammonia.

The observed separations of the three rate curves are readily accounted for by this mechanism. If formaldehyde is analysed from $(AB)_2$ while ammonia is not, it is obvious that the formaldehyde and ammonia curves cannot coincide. Also, the scheme would serve to explain, as the experiments indicate in a general way, that in the early stages of reaction less formaldehyde is analysed out of intermediates as the initial mole ratio of formaldehyde:ammonia is decreased. In excess ammonia, reaction of $(AB)_2$ with B should predominate over its reaction with A. Therefore, $(AB)_2$ should be removed rapidly from the system and its concentration be small. Hence little formaldehyde should be analysed from this intermediate. In excess formaldehyde reaction of $(AB)_2$ with A should be favoured but if the activation energy along this path be somewhat greater than along the alternative path, the rate of removal of

$(AB)_2$ should be smaller, more $(AB)_2$ should be present in the system and, therefore, more formaldehyde should be analysed from it. The reversal of this behaviour at 35° C. can be explained when the relative activation energies assigned to the formation of monomer, reaction of the dimer with formaldehyde, and reaction of the dimer with ammonia, are taken into consideration.

The question arises as to the identity of the various compounds involved as intermediates. If formaldehyde be regarded as $CH_2(OH)_2$ in aqueous solution, then a unified picture of the reaction mechanism previously given can be drawn, following the principle that formaldehyde reacts to form methylol compounds and ammonia reacts at methylol groups. According to this scheme, the dimer $(AB)_2$ may be represented as a methylol amine, $HO \cdot CH_2 \cdot NH \cdot CH_2NH_2$. This type of compound seems more probable than the one step trimerization of AB postulated by Baur and Rüetschi (1). Similarly, A_2B_3 may be represented by $H_2N \cdot CH_2 \cdot NH \cdot CH_2 \cdot NH_2$. Although hypothetical, it is analogous to methylene diamine, derivatives of which are known (5). A_3B_3 becomes the cyclo-trimethylenetriamine which has already been postulated many times (1). Hemi-hexamine is also assumed to be formed as a linear dimethylol compound which, by condensation of two molecules with loss of four molecules of water forms hexamine.

There is little point in speculating on the structure or origin of the by-product since no evidence as to its nature was obtained here. It is interesting, perhaps, that it could be a cyclic oxide formed by one mode of water elimination from the linear dimer of hemi-hexamine.

If subsequent investigation demanded it, alternative paths might be assumed to originate at the monomer AB. The type of arguments applicable would remain essentially unaltered, but the postulates would then be framed in terms of the monomer rather than the dimer.

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A RECORDING UNIT AND ELECTRONIC SHUNT SELECTOR FOR A MASS SPECTROMETER¹

By F. P. LOSSING,² R. B. SHIELDS,³ AND H. G. THODE⁴

Abstract

A direct action shunt selector has been designed that pre-selects the appropriate shunt so that widely different mass spectrometer ion currents can be recorded linearly on a standard chart. In conjunction with a linear direct current amplifier and a Leeds and Northrup Speedomax pen recorder, this unit allows rapid and accurate recording of a given mass spectrum, which can be scanned by varying either the magnetic field or the ion accelerating potential of the mass spectrometer. When used with a 180° Nier type mass spectrometer with well stabilized circuits, a precision of $\pm 0.2\%$ in measuring the ratio of CO_2^{45} and CO_2^{46} was obtained. Also, samples of xenon were investigated and the abundances of the isotopes determined.

Introduction

The usefulness of the mass spectrometer is greatly extended by the utilization of some means of fast automatic recording of the ion currents. In hydrocarbon analysis automatic recording is a practical necessity owing to the presence of many ion peaks spread over a considerable mass range. A recording system must be capable of allowing accurate measurement of ion currents varying by a factor of 1000; and, for such to be the case, it is obvious that some means must be provided for varying the sensitivity of the recording instrument so that small peaks will give a deflection of the same order of magnitude as large peaks.

Various methods of accomplishing this have been devised. Smith, Lozier, Smith, and Bleakney (3) used a galvanometer light-beam and a wide chart of photographic paper. Washburn, Wiley, and Rock (4) used four galvanometers recording simultaneously at four sensitivity levels on photographic paper. This method has been incorporated into the Consolidated Engineering Corporation mass spectrometer. Hipple, Grove, and Hickam (1) described a method using pen recording built around a Leeds and Northrup Speedomax recorder. Extension of the scale was obtained by reducing the sensitivity of the recorder as the deflection increased, thereby giving an essentially logarithmic scale. To record peak heights too large for this scale, a limit switch at the upper end of the chart changed the sensitivity level by means of a shunt. Later, J. A. Hipple developed a means for recording on a linear scale. Each peak was first traced on a logarithmic scale, and then re-traced on a linear scale, the shunt being determined by the height of the logarithmic peak.

Inghram (2) used a Brown Electronik Strip Chart Recorder whose sensitivity could be set at at least two levels. No mention is made of the method of changing sensitivity.

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The system described in this paper is similar to that used by Hipple *et al.*, in that a Speedomax pen recorder is used, but the logarithmic scale is replaced by a linear scale, and the resulting increase in deflection is handled by having a number of shunts of different sensitivities. An electronic shunt selector was designed and built which, operated by the d-c. amplifier output voltage, selects the appropriate shunt while the Speedomax pen is travelling up the forward side of the peak.

Experimental

A block diagram of the system is given in Fig. 1. The electrometer tube is a 954 acorn tube used as a space-charge tetrode feeding a stabilized, direct current, feedback amplifier. The negative output voltage is filtered to remove a-c. components and applied across the system of shunts. The sensitivity level of recording depends on the proportion of this signal that is applied to the Speedomax, and is controlled by the relays, which connect the negative lead from the Speedomax to one of the six positions along the shunt system. The amplifier output voltage is also applied to the selector circuit which determines which relay should be closed to give the sensitivity level appropriate to that voltage.

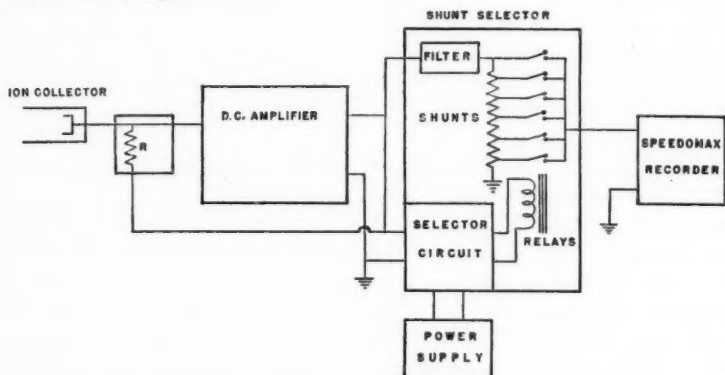


FIG. 1. Block diagram of recording system.

A schematic diagram of the shunt selector circuit is given in Fig. 2. The power supply shown for this unit delivers 250 v. at 200 ma. with a ripple of less than 0.004 v. R.M.S. The output voltage can be made almost independent of line voltage fluctuations by proper adjustment of R_2 . The heaters of all the critical tubes are connected in series and operated from this stabilized supply in order to reduce the drift.

The negative signal output voltage from the d-c. amplifier is applied to the grid of the cathode follower tube T_{10} , which isolates the d-c. amplifier from the grid current drawn by T_{11} , T_{14} , T_{17} , etc. The potentiometer R_{10} is set to give zero volts output with zero volts input. The output voltage from the cathode follower is amplified by the circuits associated with T_{11} ,

T_{12} , T_{14} , T_{15} , T_{17} , T_{19} , and T_{21} , and applied as a positive signal to the control grids of the thyratrons T_{13} , T_{16} , T_{18} , T_{20} , T_{22} . By means of the potentiometer R_{20} , the thyatron T_{13} can be set to fire at a voltage corresponding to full scale deflection on the Speedomax which is connected (at

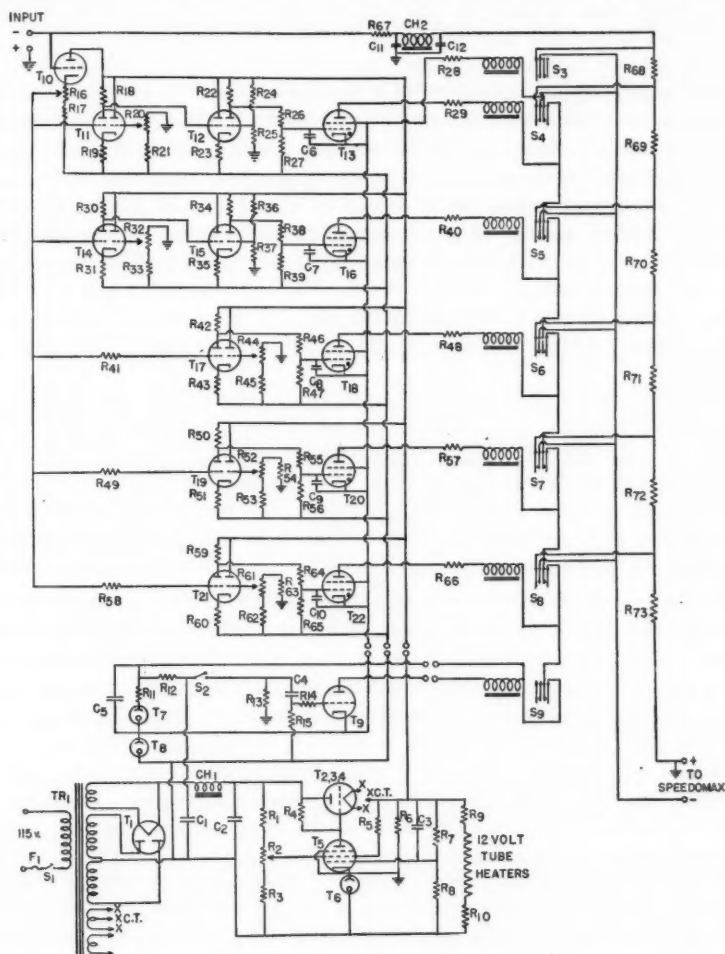


FIG. 2. Circuit of shunt selector.

no signal) to the position of maximum sensitivity by the relay S_3 . When a signal larger than this voltage is applied, thyatron T_{13} fires, closing relay S_4 and breaking the current to relay S_3 . The Speedomax is thus disconnected from its previous position and connected to the point between R_{68} and R_{69} , where its sensitivity is reduced to one-third of the previous value. In practice,

the setting of the firing voltage is made by applying a signal giving full scale deflection and advancing the helipot R_{20} until the thyatron T_{13} just fires. The other thyatrons are adjusted similarly by means of R_{32} , R_{44} , R_{52} , R_{61} to fire at full scale deflection on the other shunts.

As a large peak is scanned, the pen travels up the chart until the signal is sufficient to fire the first thyatron. At the reduced sensitivity the pen takes up a lower position, causing a step to be traced, and continues to rise with increasing signal voltage. This process is repeated until a sensitivity level is reached that allows the top of the peak to be traced. The number of this shunt can be determined by the number of steps produced in this way on the forward side of the peak (see Fig. 4). Each peak height must be multiplied by the corresponding shunt factor to give the peak height relative to the most sensitive shunt. The zero signal level for each shunt must be determined by setting the pen just above zero on the most sensitive shunt and closing the relay contacts for each shunt in turn. These zero signal levels were found to vary owing to small changes in the amount of magnetic pickup in the shunt system. Better shielding of the shunt system should eliminate this variation.

When the pen returns to the zero signal line after a peak has been traced, it closes a limit switch S_2 applying a positive pulse to the grid of tube T_9 long enough to close relay S_9 , which extinguishes the thyatrons and returns the Speedomax connection to the position of maximum sensitivity at relay S_3 . With the shunt values shown, the sensitivities on the different shunts are in the ratio 1, 1/3, 1/10, 1/30, 1/100, and 1/300, and no peak will have a height of less than 1/3 of the full width of the chart.

The position of the pen on the chart always lags behind the signal voltage by a distance depending on the slope of the side of the peak; the pen never reaches the top of the chart, since the shunt selector responds instantaneously to the signal voltage. For this reason the pen is always closer to the deflection it should have on the next shunt than it would be if the shunts were selected by means of a limit switch at the top of the chart. In spite of this, it is found occasionally, with sharp-topped peaks, that the top of a peak is traversed just after a change of shunt has occurred. In these cases the pen drops to a value on the 'trailing edge' of the peak, missing the top entirely. One solution for this contingency is that of re-scanning at a slightly increased or decreased ion current, or changing the firing voltage for that shunt. Another solution has been provided by Hipple *et al.* (1). It should be emphasized, however, that this situation arises less often with the shunt selector than with a limit switch owing to the reason given above. With mass spectrometer tubes giving square topped peaks, this difficulty is not encountered; the pen drops to the flat portion of the top.

The mass spectrometers used in this work were Nier type 180° and 90° instruments with well stabilized circuits. Scanning of the mass spectrum can be obtained by varying either the ion accelerating voltage or the deflecting field current of the mass spectrometer. Both methods were used. Smooth

variation of either the potential or the current was obtained by means of a helipot in the control circuit of the regulated supply concerned. The helipot was driven by a variable speed motor with a reversing switch so that scanning in both directions was possible. This was useful for obtaining average values when very small samples of gas were being investigated, since the ion currents may decrease with time.

Some mass spectrometer tubes may show mass discrimination when magnetic scanning is employed, while others may show mass discrimination when electrostatic scanning is employed. The availability of both methods is very useful, since, when both methods give the same results, it is likely that mass discrimination effects are at a minimum. These effects are important for isotope abundance measurements, but are not important in hydrocarbon analysis where a calibration of the instrument is made.

Results

Fig. 3 shows a typical set of xenon isotope peaks obtained at one sensitivity level, that of the most sensitive shunt. In this case the gas pressure was lowered until the highest peak (132) gave almost full scale deflection. At this low pressure, the 124 and 126 isotopes do not even register. In Fig. 4 the pressure has been increased until the 124 and 126 isotopes give an appreciable deflection, and the isotopes of greater abundance are traced on shunts of lower sensitivities because of the action of the shunt selector. In both figures the zero signal line appearing is that of the most sensitive shunt, so that the apparent rise in this line in Fig. 4 due to background between the peaks is negligible compared to the great height of these peaks when multiplied by the corresponding shunt factor.

In each case the direction of scanning was from high mass to low mass. On the leading or high mass side of each large peak may be seen the series of zigzags due to the successive selection of shunts of decreasing sensitivities, and on the low mass side of the peaks may be seen another zigzag caused by the action of the switch which returns the recorder to full sensitivity when the pen returns to the zero signal line.

The abundance of the isotopes of xenon were measured from automatically recorded spectrograms similar to Fig. 4 and are given in Table I. A more precise determination of isotopes 124 and 126 could be obtained at higher ion currents.

A sample of carbon dioxide was also investigated, and mass 45/46 ratios measured from the chart are given in Table II. For the set of 15, the per cent average deviation from the mean is $\pm 0.21\%$, and the probable error of the mean is 0.0014 or 0.05%. These results were obtained with a 180° type mass spectrometer that gave sharp-topped peaks, because of the geometry of the tube. With a 90° type mass spectrometer giving square-topped peaks,

because of wider exit slits, mass 44/46 ratios were obtained with a per cent average deviation from the mean of $\pm 0.1\%$.

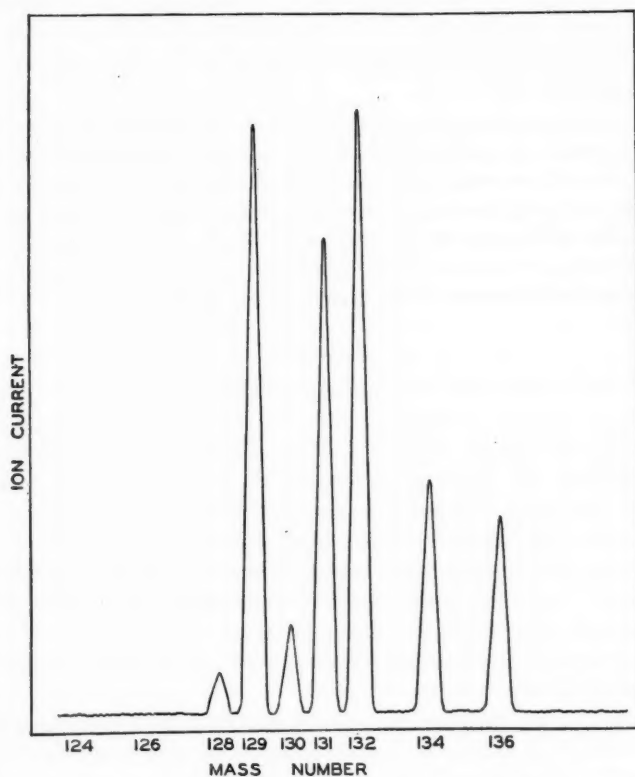


FIG. 3. Xenon isotopes recorded at one sensitivity level.

TABLE I
PERCENTAGE CONSTITUTION OF XENON

	Mass abundance								
	124	126	128	129	130	131	132	134	136
Trial 1	0.095	0.089	1.925	26.30	4.050	21.20	26.90	10.55	8.98
Trial 2	0.096	0.088	1.915	26.12	4.060	21.28	26.95	10.51	8.91
Trial 3	0.094	0.086	1.910	26.30	4.050	21.25	26.95	10.50	8.90
Average	0.095	0.088	1.917	26.24	4.053	21.24	26.93	10.52	8.93
Deviation	± 0.001	± 0.001	± 0.006	± 0.08	± 0.004	± 0.03	± 0.02	± 0.02	± 0.03

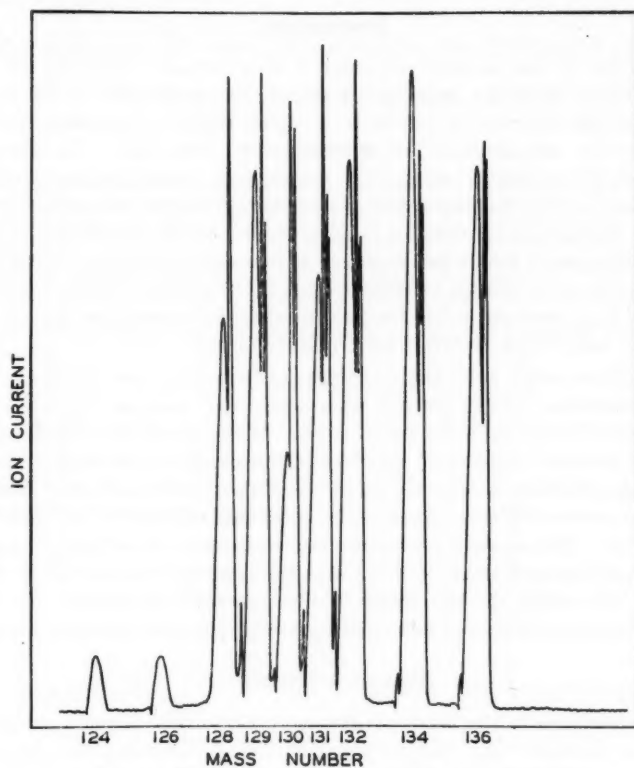


FIG. 4. Xenon isotopes recorded using shunt selector.

TABLE II
RATIO OF CO_2^{45} TO CO_2^{46}

Peak height, cm.		Ratio 45/46	Deviation
45	46		
57.15	19.52	2.928	0.003
57.24	19.58	2.924	0.001
57.06	19.52	2.923	0.002
57.18	19.50	2.931	0.008
56.94	19.48	2.923	0.002
56.64	19.42	2.917	0.008
56.70	19.50	2.910	0.015
57.00	19.50	2.923	0.002
56.94	19.32	2.947	0.022
56.76	19.32	2.938	0.013
56.64	19.40	2.920	0.005
56.40	19.30	2.922	0.003
56.55	19.32	2.927	0.002
56.55	19.32	2.927	0.002
56.40	19.32	2.919	0.006
		Average 2.925	± 0.0062

Discussion

In addition to the obvious advantages of automatic recording for hydrocarbon analysis with the mass spectrometer, its application to the measurement of isotope abundance results in a higher degree of precision than that obtainable by measurement of galvanometer deflection. To obtain the abundances of the xenon isotopes by the manual method takes considerable time, during which changes in the gas pressure, filament characteristics, and electronic circuit characteristics might occur. With automatic recording the nine isotopes of xenon are scanned in two minutes or less, during which time the amount of change in these factors is very much smaller. The ratio of any two isotopes can be rapidly and accurately measured by scanning them alternately until 10 or 20 ratios have been obtained.

The question arises as to the usefulness of recording equipment for routine isotope abundance measurements where only two isotopes are involved, as for example C^{13} , N^{15} , and O^{18} assay work. If 1% accuracy is sufficient it is debatable whether automatic recording equipment is justified. However, where high precision is required as in the determination of small differences in isotopic content of two samples, the recording equipment has been found most useful. This work involves the determination of exchange factors for isotopic reactions and small differences in the isotopic constitution of the light elements, depending on the source. The precision obtainable for routine O^{18} determinations has been extended to 0.1% of its normal concentration.

Acknowledgments

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THE KINETICS OF THE FORMATION OF ETHANOLAMINES¹

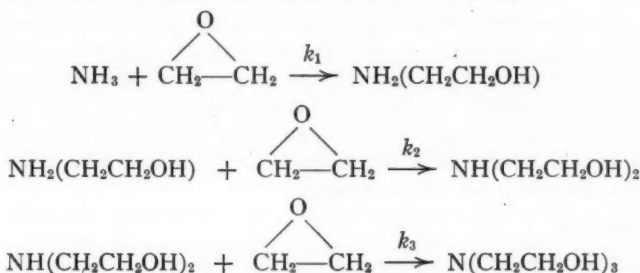
BY C. POTTER² AND R. R. McLAUGHLIN³

Abstract

The formation of ethanolamines from ethylene oxide and ammonia is a case of simultaneous, consecutive, competitive second order reactions. The results obtained show the time at which to stop a reaction for a maximum yield of any one of the three products. It is shown that as the reaction proceeds from ammonia to monoethanolamine to diethanolamine to triethanolamine the velocity constants are in the ratio of 1 : 6 : 4 for the three reactions. The values of the velocity constants are determined graphically. From these values an energy of activation of 16,600 cal. is calculated and is the same for each step. There is an indication that a tetraethanol-ammonium hydroxide is slowly formed.

Introduction

This research on the kinetics of formation of ethanolamines was undertaken to find the data necessary for the calculation of the maximum production of diethanolamine by a continuous process. The reactions taking place when ethylene oxide reacts with ammonia are (5, 6, 7, 8, 9, 15):



Other methods involve the use of ethylene chlorohydrin (17) in place of ethylene oxide, ammonium salts (10, 12), and recently a gas phase reaction has been patented.

The mathematical treatment covering the theory of consecutive competitive reactions as exemplified by the experimental work presented here, has been presented (11) and the following equations developed:

$$\begin{aligned} y_1 &= \frac{y_0}{1 - \alpha} (y_0^{\alpha-1} - 1) \\ y_2 &= \alpha y_0 \left[\frac{y_0^{\beta-1}}{(\alpha - \beta)(1 - \beta)} - \frac{y_0^{\alpha-1}}{(\alpha - \beta)(1 - \alpha)} - \frac{1}{(\alpha - 1)(\beta - 1)} \right] \\ 3 - Y &= Ay_0^\alpha + By_0^\beta + Cy_0 \end{aligned}$$

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont. Condensed from a portion of a thesis submitted in partial fulfillment of requirements for the degree of Ph.D.

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$$A = \frac{1}{1-\alpha} - \frac{\beta}{(\alpha-\beta)(1-\alpha)} \quad B = \frac{\alpha}{(1-\beta)(\alpha-\beta)}$$

$$C = 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)}$$

$$Y = y_1 + 2Y_2 + 3Y_3$$

$$= 3 - 3y_0 - 2y_1 - y_2$$

$$y_3 = 1 - y_0 - y_1 - y_2$$

$$\frac{k_2}{k_1} = \alpha; \quad \frac{k_3}{k_1} = \beta$$

y_0 = moles of ammonia present per mole original ammonia

y_1, y_2, y_3 = moles of amine per mole original ammonia

Y = moles ethylene oxide used up per mole ammonia

k_1, k_2, k_3 = velocity constants.

Experimental Procedure

Epilome

The rate at which ethylene oxide reacts with ammonia was determined as follows. A weighed amount of ethylene oxide in a small test-tube was dropped into a larger one containing a definite quantity of ammonium hydroxide. The larger tube was tightly stoppered and placed in a constant temperature bath for a definite period. At the end of the desired time, the tube containing the reaction mixture was opened and rinsed into a volumetric flask containing hydrochloric acid for stopping the reaction, and the resulting solution was analysed for ammonia and ethanolamines.

(a) The Reaction

Standardized ammonium hydroxide solution was measured into the larger test-tube. Ethylene oxide from a cylinder was passed through a soda-lime tower, through a downward spiral ice condenser, and collected in slight excess of the desired amount in a small weighed test-tube placed upright in a beaker (or other suitable container). The test-tube and beaker were placed on the balance with the desired weight on the other pan and evaporation of the excess ethylene oxide allowed to take place. When the correct weight had been reached the test-tube was quickly removed and dropped into the ammonium hydroxide solution, the time observed, the larger tube sealed and the stopper wired down. Finally, the tube was placed in a constant temperature bath. It was shaken at frequent intervals to ensure complete mixing.

When known amounts of ethylene oxide and ammonia were mixed and the reaction allowed to go to completion, the experiment was called a static run. When the reaction had been stopped before it had reached completion and the time of reaction measured, the experiment was called a kinetic run.

Kinetic runs were made at 10°, 20°, and 30° C. Static runs were made at room temperature and the samples allowed to stand for four days before being analysed.

The kinetic run at 10° C. was started with 6.2 gm. ethylene oxide, 10 ml. 3.493 *N* ammonium hydroxide and 10 ml. water. The kinetic runs at 20° and 30° C. were started with the same amounts of reagents but with 25 ml. water instead of 10 ml. in order to retard by dilution the reaction rate. In the static runs varying quantities of ethylene oxide were mixed with a fixed quantity of ammonium hydroxide, viz.: 10 ml. 3.613 *N* ammonium hydroxide and 25 ml. water. After reaction had taken place for the desired time in the kinetic runs, the samples were rinsed into a 250 ml. volumetric flask, containing 25 ml. 12 *N* hydrochloric acid used to stop the reaction (twice the total number of moles of original ammonia and ethylene oxide present) and made up to volume. In the static runs, hydrochloric acid to stop the reaction was unnecessary, since the reaction would be virtually complete because it had been allowed to take place for four days.

It will be noted from this description that the points on any one of the curves of Fig. 1 are based upon separate reaction mixtures for each point.

(b) *Analytical Procedure*

(i) *Aeration*.—The mixture of ammonia and amines was analysed by aerating (16) the sample to remove the ammonia and separating the amines by the Hinsberg method, using *p*-bromobenzenesulphonyl chloride. Air, washed by passing through 10% sulphuric acid, was passed through the sample and then through a 5% boric acid solution to absorb the ammonia evolved.

(ii) *Ammonia separation*.—A test-tube charged with a 25 ml. sample of reaction mixture was connected to a second test-tube containing 50 ml. of 5% boric acid solution. Saturated potassium carbonate solution (10 ml.) was added to the sample. Air was drawn very slowly through the apparatus for five minutes by means of suction and then rapidly for 30 min. Finally the sample tube was immersed to a depth of 2 in. in a 400 ml. beaker of water (100° C.) and aspiration continued for another 30 min., without further heating of the water-bath.

The ammonia absorbed in the boric acid was determined by titration with standard sulphuric acid, using a mixed bromocresol green and methyl red indicator.

(iii) *Amine separation*.—The contents of the sample tube were neutralized to a methyl orange end-point with concentrated hydrochloric acid, and 2 gm. sodium bicarbonate, 25 ml. of acetone, and 2 gm. of *p*-bromobenzenesulphonyl chloride added. The tube was placed in a hot water-bath and the acetone slowly evaporated, with occasional stirring. The solution was then cooled, and 10 ml. 10% wt./vol. sodium hydroxide, 20 ml. alcohol, and a small piece of porous tile added. The tube was then returned to the water-bath for evaporation of the alcohol.

From this point the separation of mono- and diethanolamine was made with chloroform as described by Shupe (14). The stopcocks on the separating funnels were greased with colloidal graphite.

(iv) *Correction of analytical figures.*—Having developed the method just described as the most suitable available for the reaction mixtures involved, we analysed a series of samples from a kinetic run by this method. Artificial

TABLE I
ANALYTICAL CORRECTIONS

Moles ammonia	Moles monoethanolamine per mole ammonia			Moles diethanolamine per mole ammonia		
	Present	Found	Correction	Present	Found	Correction
0.90	0.0690	0.0689	+0.0001	0.0210	0.0211	-0.0001
0.70	0.1120	0.1091	+0.0029	0.0960	0.0793	+0.0167
0.50	0.0970	0.0952	+0.0018	0.1390	0.1314	+0.0076
0.30	0.0650	0.0700	-0.0050	0.1080	0.1040	-0.0040
0.10	0.0310	0.0431	-0.0121	0.0350	0.0417	-0.0067

mixtures of ammonia, monoethanolamine, diethanolamine, and triethanolamine corresponding with the results obtained were made up and analysed in the same way. The differences between the known and analytical values appear in Table I, and were used as corrections in all reported results. The values for ammonia required no correction.

Experimental Results

The experimental results are shown in Fig. 1.

At this point it could be seen that the system was not so simple as originally postulated for the full course of the reaction since the concentration of ammonia should have been zero at three moles of ethylene oxide (Fig. 2). The experimental results showed that it approached zero at four moles of ethylene oxide. This would be the case if the ethylene oxide were used up by another reaction, say the formation of tetra-ethanolamine. A search of the literature did not yield much information in this regard (3, 9, 17). Such a reaction is possible by analogy since trimethylamine will react with ethylene oxide to give choline.

In view of the difficulty of interpreting the experimental results more information was sought. First, a static run was conducted using diethanolamine and ethylene oxide. The results were plotted on an ethylene oxide base (Fig. 3). The graph seems to confirm the hypothesis that a fourth compound was formed since the concentration of diethanolamine approaches zero at two moles of ethylene oxide instead of one. It can also be seen that this reaction must be very slow since the curve is very close to the straight line joining one mole of ethylene oxide to one mole of diethanolamine. The second compound would not show up to any appreciable extent until late in

MONOETHANOLAMINE AND DIETHANOLAMINE
PER MOLE AMMONIA

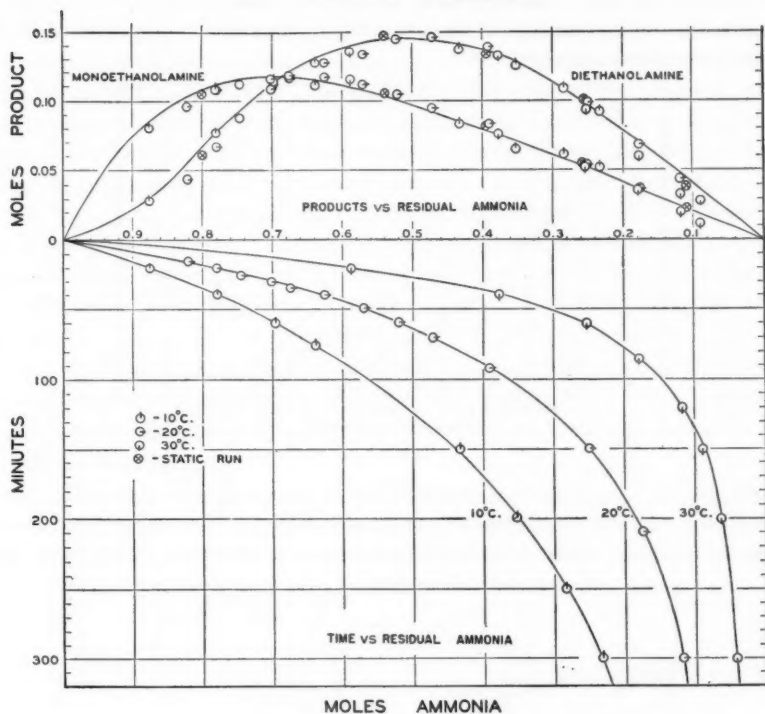


FIG. 1

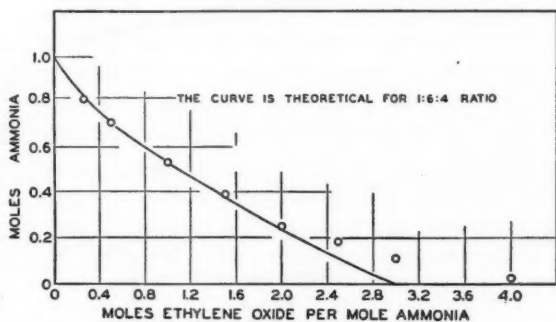


FIG. 2

the reaction. In other words over the early period of a reaction involving ethylene oxide and diethanolamine the ratio at which these two substances would be used up is almost 2 to 1.

Aqueous triethanolamine was mixed with ethylene oxide. Considerable heat was generated, showing that a reaction took place, but attempts to isolate the chloroplatinate of the quaternary ammonium base resulted in the formation of viscous orange oils.

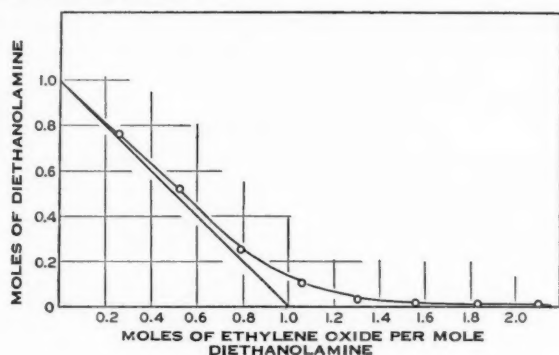


FIG. 3

Finally, the solutions from the static run on ammonia were titrated potentiometrically and the results were plotted as in Fig. 4. This showed the formation of a highly basic substance, probably a quaternary ammonium base.

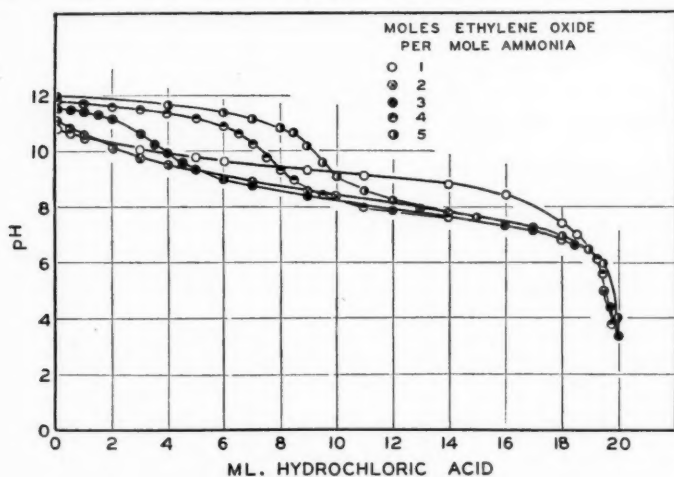


FIG. 4

Controls on the ethanolamines showed them all to be weakly basic. The experiment also indicated that the formation of the quaternary base was not quantitative since not all the weaker bases were converted even at five moles of ethylene oxide per mole of ammonia. In this connection, Fig. 3 shows that the quaternary base does not occur in any appreciable quantity until late in the reaction.

Treatment of Experimental Results

From the foregoing, and from a study of the graphs, it was decided that the over-all reaction, as first postulated, did not give a complete picture of what was taking place in the system. A study of the two graphs (Figs. 2 and 3), plotted on an ethylene oxide base, shows that the effect of the products, other than those postulated, does not exert itself to any appreciable extent until late in the reaction, and the effective rate of formation of these products was slow in comparison with the main reactions. It was, therefore, decided to limit the analysis of the curves to a point where the effect of the secondary products was still small. This was entirely in keeping with the practical aspects of the problem since, at the outset, it was desired only to find the conditions for calculating when the maximum yield of diethanolamine would occur.

The mathematical analysis of the curves was made up to a point where 60% of the ammonia had entered the reaction. All amines other than ammonia, mono-, and diethanolamine were considered to be triethanolamine in the material balance.

TABLE II
SLOPES TAKEN FROM AMMONIA-TIME CURVES IN FIG. 1

%	10° C.	20° C.	30° C.
0.8	0.004969	0.009466	0.02232
0.6	0.003230	0.005920	0.01460
0.4	0.001838	0.003197	0.00800

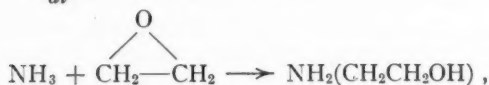
By a process of trial and error the velocity constant ratios $K_1 : K_2 : K_3$ or $1 : \alpha : \beta$ were found to be 1 : 6 : 4 for all temperatures and also for the static run. These calculated curves are represented by the lines in the upper part of Fig. 1 and the points represent experimental values.

There are certain cases where the ratios of the velocity constants could possibly be in the ratio of small whole numbers. In a four step substitution, where the reaction takes place in the ratio of the probability of collision the ratios would be $1 : \frac{3}{4} : \frac{1}{2} : \frac{1}{4}$. Other cases are discussed by R. M. Fuoss (4) in his paper.

Having fixed the ratio of the velocity constants as belonging to a 1 : 6 : 4 system and having assumed that any amines other than ammonia, mono-, and diethanolamine shall be considered as triethanolamine, it becomes possible to evaluate the velocity constants at the temperatures at which the reaction was studied.

The problem was solved by a graphical solution of:

$$\frac{dx}{dt} = k_1(a - x)(b - Y)$$



a = original ammonia,

b = original ethylene oxide,

x = ammonia going into reaction.

For 1 : 6 : 4 ratios, calculated points (Table III) give rise to the curves in Fig. 1.

TABLE III

Ammonia present	Ammonia used up	Ethylene oxide used up
y_0	x	Y
0.8	0.2	0.3172
0.6	0.4	0.8402
0.4	0.6	1.5048

Sample Calculation

Ten millilitres of ammonium hydroxide contain 0.0349 equivalents (about 6%, specific gravity 0.973).

	10° C.	20° and 30° C.
Wt. of ammonia solution	9.73	9.73
Wt. of water	10.00	25.00
Wt. of ethylene oxide	6.20	6.20
	25.93 gm.	40.93 gm.

Since for this calculation actual concentrations are required Y must be multiplied by $0.03493/25.93 = 0.001347$ for 10° C., and $0.03493/40.93 = 0.0008535$ for 20° and 30° C.

The concentration coefficients for $(a - x)$ and dx cancel since they appear on both sides of the equation.

$$b = \frac{6.20}{(44.05)(25.93)} = 0.005428 \text{ moles/gm. for } 10^\circ \text{ C.}$$

$$b = \frac{6.20}{(44.05)(40.93)} = 0.003444 \text{ moles/gm. for } 20^\circ \text{ C. and } 30^\circ \text{ C.}$$

Solving for k_1 in $\frac{dx}{dt} = k_1(a - x)(b - Y)$

y_0	k_1 at 10° C.	k_1 at 20° C.	k_1 at 30° C.
0.8	1.243	3.730	8.794
0.6	1.253	3.616	8.921
0.4	1.351	3.699	9.258
	1.282	3.681	8.991 gm./mole/min.

$k = Ze^{-E/RT}$ Arrhenius equation,

k = velocity constant,

E = energy of activation,

Z = collision or orientation factor,

$$E = \frac{(RT'T'')}{(T'' - T')} 2.303 \log \frac{k''}{k'}$$

$E_{10^\circ \text{ to } 20^\circ \text{ C.}}$ 17,400 cal.

$E_{10^\circ \text{ to } 30^\circ \text{ C.}}$ 16,700 cal.

$E_{20^\circ \text{ to } 30^\circ \text{ C.}}$ 15,800 cal.

Average 16,600 cal.

In view of the fact that temperature variations did not alter the ratio of the products, the energy of activation is the same for each step and is 16,600 cal. per mole.

An explicit solution for the value of k_1 is possible by substituting for Y in terms of x . It would be tedious and requires finding six roots in this case.

From the values derived, it is possible to solve the problem for any other concentration and temperature conditions by a graphical integration of

$$\frac{dx}{dt} = k_1 (a - x) (b - Y)$$

$$k_1 t = \int \frac{dx}{(a - x) (b - Y)}$$

k_1 can be found since the energy of activation is known. The values of a , b , and x can be arbitrarily chosen. From Tables II and III sufficient values of

$\frac{1}{(a - x) (b - Y)}$ could be found to calculate from the equations points to draw

a curve over the period 0 to x . By finding the area under this curve the solution for the time of reaction can be readily calculated.

Acknowledgments

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THE KINETICS OF CONSECUTIVE SECOND ORDER REACTIONS¹

BY C. POTTER² AND W. C. MACDONALD³

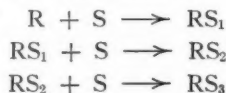
Abstract

A study of consecutive competitive second order reactions is reported. It is shown that identical equations can be obtained by two different approaches. A static method is described where equations are developed by considering the changes brought about in the system by the addition of small quantities of one of the reactants. Equations are also developed from the point of view of kinetics. These equations express the concentrations of the products as functions of the concentration of one of the reactants and the ratio of the velocity constants.

An interesting case of chemical kinetics is that of consecutive competitive second order reactions. One set of theoretical equations was obtained by Fuoss (1) by considering what happens to a system when a differential quantity of one of the reactants is added. Another set of equations can be developed by the method of F. Martin and Fuchs (2) by considering the kinetics of the system. This paper shows that the two methods lead to identical equations.

Method of Differential Material Balances

If the chemical equations are represented by:



it has been shown that the following set of equations can be developed to describe the system (1).

$$\begin{aligned} y_1 &= \frac{y_0}{1-\alpha} [y_0^{\alpha-1} - 1]; \quad \alpha \neq 1, \\ y_2 &= \alpha y_0 \left[\frac{y_0^{\beta-1}}{(\alpha-\beta)(1-\beta)} - \frac{y_0^{\alpha-1}}{(\alpha-\beta)(1-\alpha)} + \frac{1}{(1-\alpha)(1-\beta)} \right]; \quad \beta \neq 1, \\ 3 - Y &= Ay_0^\alpha + By_0^\beta + Cy_0, \\ A &= \frac{1}{1-\alpha} - \frac{\beta}{(\alpha-\beta)(1-\alpha)}, \\ B &= \frac{\alpha}{(\alpha-\beta)(1-\beta)}, \\ C &= 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)}. \end{aligned}$$

¹ Manuscript received in original form October 30, 1946, and, as revised, March 28, 1947.

Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont. Condensed from a portion of a thesis submitted in partial fulfilment of the requirements for the degree of Ph.D.

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³ Associate Professor.

The mole fractions of R, RS_1 , and RS_2 are represented by y_0 , y_1 , and y_2 . The ratio of the reaction probabilities is $1 : \alpha : \beta$, and Y is the mole fraction of the S constituent.

Kinetic Method

The kinetic method of approach leads to the same conclusions on the assumption that all the reactions are of the second order type.

Let k_1 , k_2 and k_3 be the velocity constants,

t = time,

a = initial concentration of R,

b = initial concentration of S,

Y = amount of S which has entered the reaction,

x = amount of R which has entered the reaction,

y_1 , y_2 , y_3 be the concentration of the products.

A material balance requires that:

$$x = y_1 + y_2 + y_3$$

$$Y = y_1 + 2y_2 + 3y_3.$$

The rate equations are:

$$\frac{dx}{dt} = k_1(a - x)(b - Y),$$

$$\frac{dy_1}{dt} = k_1(a - x)(b - Y) - k_2y_1(b - Y),$$

$$\frac{dy_2}{dt} = k_2y_1(b - Y) - k_3y_2(b - Y),$$

$$\frac{dy_3}{dt} = k_3y_2(b - Y).$$

Eliminating dt and integrating between 0 and x gives

$$y_1 = k_1(a - x) \left[\frac{1}{k_2 - k_1} + \frac{1}{k_1 - k_2} \left(\frac{a}{a - x} \right)^{\frac{k_1 - k_2}{k_1}} \right],$$

where

$$\frac{k_2}{k_1} \neq 1.$$

Similarly,

$$y_2 = k_1k_2(a - x) \left[\frac{1}{(k_2 - k_1)(k_3 - k_1)} + \frac{1}{(k_1 - k_2)(k_3 - k_2)} \left(\frac{a}{a - x} \right)^{\frac{k_1 - k_2}{k_1}} + \frac{1}{(k_1 - k_3)(k_2 - k_3)} \left(\frac{a}{a - x} \right)^{\frac{k_1 - k_3}{k_1}} \right].$$

From the symmetry of the equations any y_i can be written down directly.

For y_3 , if k_4 is zero,

$$y_3 = k_1k_2k_3(a - x) \left[\frac{1}{(k_2 - k_1)(k_3 - k_1)(-k_1)} + \frac{1}{(k_1 - k_2)(k_3 - k_2)(-k_2)} \left(\frac{a}{a - x} \right)^{\frac{k_1 - k_2}{k_1}} + \frac{1}{k_1k_2k_3} \left(\frac{a}{a - x} \right) \right].$$

When $k_i/k_1 = 1$ the integrations lead to logarithmic expressions.

In general it is convenient to use the ratio of the rate constants and to express the concentrations in moles per mole of the original R constituent.

Thus, $a = 1$

$$k_2/k_1 = \alpha$$

$$k_3/k_1 = \beta$$

$$y_0 = 1 - x \text{ moles of R per mole of original R used,}$$

$$y_1 = \frac{y_0}{1 - \alpha} (y_0^{\alpha-1} - 1),$$

$$y_2 = \alpha y_0 \left[\frac{y_0^{\beta-1}}{(\alpha - \beta)(1 - \beta)} - \frac{y_0^{\alpha-1}}{(\alpha - \beta)(1 - \alpha)} + \frac{1}{(\alpha - 1)(\beta - 1)} \right],$$

$$y_3 = 1 - y_0 - y_1 - y_2,$$

$$Y = y_1 + 2y_2 + 3y_3,$$

$$= 3 - 3y_0 - 2y_1 - y_2,$$

$$3 - Y = Ay_0 + By_0 + Cy_0,$$

$$A = \frac{2}{1 - \alpha} + \frac{\alpha}{(1 - \alpha)(\beta - \alpha)} \equiv \frac{1}{1 - \alpha} - \frac{\beta}{(\alpha - \beta)(1 - \alpha)},$$

$$B = \frac{\alpha}{(1 - \beta)(\alpha - \beta)},$$

$$C = 3 + \frac{2}{\alpha - 1} + \frac{\alpha}{(\alpha - 1)(\beta - 1)} \equiv 1 - \frac{\alpha}{1 - \alpha} + \frac{\alpha\beta}{(1 - \alpha)(1 - \beta)}.$$

Thus it is seen that the kinetic and static approaches lead to the same equations for the system.

The next question that arises is: what is the significance of $\alpha = k_2/k_1$ and $\beta = k_3/k_1$, where α and β are defined as the reaction probabilities?

Writing the Arrhenius equation as $k = z e^{-E/RT}$, where z includes all the requirements that the reacting molecules must have other than those of energy, k is the rate constant, and E the energy of activation.

$$k_1 = z_1 e^{-\frac{E_1}{RT}},$$

$$k_2 = z_2 e^{-\frac{E_2}{RT}},$$

$$\alpha = \frac{k_2}{k_1} = \frac{z_2}{z_1} e^{\frac{(E_1 - E_2)}{RT}}.$$

When the successive reactions make similar replacement of bonds, the energies of activation may be nearly equal for each step. In this case

$$1 : k_2/k_1 : k_3/k_1 = 1 : z_2/z_1 : z_3/z_1 = 1 : \alpha : \beta$$

and the equations governing y_i and Y will be independent of temperature. This would indicate that the difference in reaction probabilities is due only to the orientation requirements of the reacting species of molecules.

On the other hand, if each step has a different energy of activation, then the values of α and β will no longer be independent of temperature:

$$\alpha = \frac{k_2}{k_1} = \frac{S_2}{S_1} e^{\frac{E_1 - E_2}{RT}},$$

$$\alpha' = \frac{k_2'}{k_1'} = \frac{S_2'}{S_1'} e^{\frac{E_1' - E_2'}{RT}},$$

$$\frac{\alpha}{\alpha'} = e^{\frac{E_1 - E_2}{R} \left(\frac{T' - T}{TT'} \right)}.$$

It is of interest to note that the equations governing the intermediates, y_1 , and y_2 , depend only on the way in which these products are formed and disappear, and not on the number of steps involved after their disappearance. On the other hand, this reasoning does not hold for the equations governing the disappearance of R and S, nor for the formation of the final product. Thus if the values of the intermediate y_i 's are plotted against y_0 the shapes of the curves do not depend on the number of steps involved.

In order to determine the ratio of the rate constants, it is not necessary to find the rates of reaction but merely to set up several experiments in which a fixed quantity of R is reacted with different quantities of S. Analysis of the resulting mixtures will yield considerable information. When the values of y_i are plotted against y_0 it is possible to tell whether the reaction proceeds as postulated by the way in which the experimental curves fit the family of theoretical curves. The ratio of the velocity constants can be found by fitting the experimental results to theoretical curves. If the experimental curves shift with temperature, then it will be realized that the energy of activation is not the same for each step.

When R is ammonia and the reaction involves substituting S radicals for hydrogen, there may be some doubt whether a quaternary ammonium base is formed, as in the formation of ethanolamines (3). By plotting the experimental results for the y_i 's against Y it will be realized that if they approach zero at $Y = 4$ moles, then a quaternary ammonium base is likely to have been formed, but on the other hand if they approach zero at $Y = 3$ moles, then it is not likely that a fourth amine is present.

If it is desired to find the absolute values of the velocity constants, then it will be necessary to run a series of kinetic experiments. From the results, the ratios of the velocity constants may be found as before. By plotting the values of x against time t , the value of k_1 can be found from $\frac{dx}{dt} = k_1(a - x)(b - Y)$. In general a graphical solution will be necessary since an explicit solution of the above equation except in special cases is very cumbersome.

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Fractionation of the Reaction Product of Linseed Oil and Glycerol

This paper presents the results of attempts to separate the reaction product of linseed oil and glycerol into fractions of different unsaturation, which may be useful in the production of ester-type resins and other industrial applications (4).

Reaction Between Linseed Oil and Glycerol.—The literature on the reaction between glyceride oils and glycerol has been reviewed by Goldsmith (4); Blagonravova *et al.* (2) and Feuge and Bailey (3) have published papers on the composition of the reaction product.

The reaction was carried out as follows: the amount of B.P. glycerol shown in Table I and 300 gm. alkali-refined linseed oil (iodine no. = 185.0, saponification no. = 197.0, average number of double bonds per fatty acid radical = 2.08) were placed in a 1 litre Pyrex three-necked flask, fitted with thermometer, stirrer, and air-cooled reflux condenser. The mixture was heated to 240° C., 0.3 gm. calcium acetate monohydrate added, and the temperature maintained at 240° C. for one hour. The mixture was allowed to cool to room temperature and the two resulting liquid layers separated, the lower layer consisting of glycerol and a trace of ester, and the upper layer consisting of the partial ester and some free glycerol. The upper layer was used as obtained for the subsequent fractionation experiments.

Table I shows some of the properties of representative ester layers obtained by using different proportions of glycerol, the average number of double bonds per fatty acid radical being indicated by the symbol *N*.

TABLE I

Type	Glycerol, gm.		Ester layer			
	Used	Recovered	Weight, gm.	Iodine No.	Saponification No.	<i>N</i>
A	300	209.1	377.5	145.5	157.0	2.05
B	225	134.8	374.1	144.0	157.2	2.03
C	150	64.3	376.9	143.7	159.1	2.00
D	75	10.6	361.7	149.2	162.3	2.03
E	45	2.1	336.7	159.6	173.7	2.03

For economic reasons it would be imperative that the glycerol recovered be re-used in subsequent reactions, and in order to ascertain that on continued re-use no accumulation of ether-type compounds in the glycerol took place,

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the hydroxyl content of the recovered glycerol from Type *C* reactions was determined by the method of Ogg, Porter, and Willits (6). It was found that the original glycerol had hydroxyl content = 54.7%; after being used two and three times the values were 54.0% and 55.2% respectively.

Fractionation of the Reaction Product.—Attempts were made to separate the reaction product into fractions of different degree of unsaturation by three methods, involving (a) distribution in two-phase liquid systems, (b) fractional crystallization of the reaction product, and (c) fractional crystallization of a solution of the reaction product. No appreciable separation was obtained by Method (a), but a certain degree of separation resulted using Method (b). Using crystallization temperatures from 25° to 5° C., solid fractions were obtained ranging from 10 to 40% by weight of the starting sample, and with a value for $N = 1.7 \pm 0.1$. Using Method (c), however, an appreciable degree of separation was obtained. The general procedure was as follows: a sample of the reaction product was dissolved in a solvent, and the solution allowed to stand at the temperatures noted for from 24 to 48 hr., until crystallization was apparently complete. The solid fraction was separated by filtration through Whatman No. 4 filter paper and its characteristics determined, from which those of the liquid fractions may be calculated. The results are summarized in Table II, in which the weights of the solid fractions are those obtainable from 100 gm. of the reaction product.

TABLE II

Type	Temp., °C.	Solvent	Amount, gm.	Solid fraction			
				Weight, gm.	Iodine No.	Saponifi- cation No.	<i>N</i>
<i>A</i>	5	Carbon tetrachloride	100	8.7	68.8	140.5	1.08
<i>A</i>	5	Benzene	100	8.5	93.5	150.0	1.38
<i>A</i>	5	Chloroform	100	20.0	103.6	147.4	1.56
<i>A</i>	5	Methanol	100	13.8	118.0	161.0	1.62
<i>A</i>	5	95% methanol, 5% water	100	16.3	119.6	160.9	1.65
<i>A</i>	5	Ethyl acetate	100	19.2	102.8	137.4	1.66
<i>A</i>	5	95% acetone, 5% water	100	19.0	116.8	154.1	1.68
<i>A</i>	5	Acetone	100	15.5	115.2	150.0	1.70
<i>A</i>	5	Diethylether	100	17.0	116.6	138.0	1.87
<i>C</i>	5	Carbon tetrachloride	100	11.2	74.3	150.1	1.10
<i>D</i>	5	"	100	14.0	104.6	159.0	1.46
<i>E</i>	5	"	100	18.8	125.7	166.6	1.67
<i>A</i>	5	"	75	8.9	78.6	148.2	1.17
<i>A</i>	5	"	50	9.8	97.2	159.6	1.35
<i>A</i>	5	"	25	32.6	124.1	157.0	1.75
<i>A</i>	0	"	100	13.3	83.4	143.2	1.29
<i>A</i>	0	"	75	17.7	102.5	147.9	1.53
<i>A</i>	-5	"	100	23.6	95.2	137.0	1.54
<i>A</i>	-10	"	150	20.4	98.4	123.1	1.77

In order to determine the range of this method of fractionation, similar crystallizations were carried out, using as starting material samples of Type *A* reaction products which had already been fractionated to some extent. The

results are summarized in Table III, in which the weights of the solid fractions are those obtainable from 100 gm. of the starting material.

TABLE III

Starting material			Solvent	Temp. ° C.	Solid fraction			
Iodine No.	Saponification No.	N			Weight, gm.	Iodine No.	Saponification No.	N
155.6	157.9	2.18	30 gm. CH ₃ OH	-20	0	—	—	—
149.4	156.1	2.12	10 gm. "	-10	30.0	135.0	152.0	1.96
153.4	161.6	2.10	100 gm. CCl ₄	-20	55.5	143.5	156.2	2.04
151.6	162.0	2.07	50 gm. "	-10	48.4	148.4	162.6	2.02
146.0	157.9	2.05	50 gm. "	-5	17.0	127.6	152.5	1.85
120.9	154.0	1.74	150 gm. "	25	28.2	94.0	154.7	1.34
94.0	154.7	1.34	200 gm. "	30	46.1	60.0	143.0	0.93
60.0	143.0	0.93	300 gm. "	30	40.0	18.2	134.4	0.30
46.6	140.0	0.74	400 gm. "	30	50.8	12.0	116.2	0.22

Discussion.—Although fractional crystallization without a solvent is a relatively inefficient method of separation, it would require a minimum of equipment in practice, and the fractions produced might serve as starting materials for crystallization from a solvent.

It is interesting to note that fractionation takes place with respect to fatty acid content as well as unsaturation, since fractions of low unsaturation also have a low saponification number.

It is suggested that the ideas outlined here might be adaptable to drying oils other than linseed oil, especially those that contain comparatively large amounts of fatty acids of low unsaturation, such as soya bean oil.

Analytical Methods.—The iodine numbers of the fractions were determined by the Hanus method (1); the saponification numbers were determined by the decigram procedure described by Marcali and Rieman (5); from these data the average number of double bonds per fatty acid radical was calculated.

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